

# Polymer Supported Catalysts in Organic Reactions

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**Abstract - Phase Transfer Catalysis (PTC) is an effective approach for the synthesis of organic reactions involving two immiscible-phased molecules. The purpose of this work is to develop several soluble and insoluble phase-transfer catalysts for the heterogeneous synthesis of various chemical compounds utilizing ultrasonic energy. Although chemical reactants reside in immiscible phases, phase-transfer catalysts may move one of the reactants over the interface into the other phase where the reaction happens, resulting in moderately high conversion and selectivity for the desired product. In general, quaternary onium salts, such as tetra alkyl ammonium or phosphonium salts (Q<sup>+</sup> X<sup>-</sup>), are effective catalysts for accelerating the expansion of phase-transfer catalysis, a promising method for organic synthesis. It requires a simple experimental approach, mild reaction conditions, expensive and environmentally friendly ingredients and solvents, and has the potential for large-scale production. Nowadays, phase-transfer catalysis seems to be a leading synthetic approach, appreciated not only in many fields of organic chemistry, but also in a vast array of commercial applications.**

**Keywords - Phase Transfer Catalysis (PTC), Phase Transfer Catalysts, Organic Reactions, Immiscible Phases**

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## INTRODUCTION

### ➤ Overview:

New synthetic processes that are friendlier to the natural world have been spawned as a direct result of the growing importance of "green chemistry" in the process of organic compound formation. Green chemistry is a method that aims to solve pollution and sustainability problems by developing chemical reactions that are less harmful to the environment. In order to be considered eco-friendly or green, organic synthesis has to fulfil at least some of the following criteria: avoiding waste, being atom efficient, avoiding the use and production of toxic and dangerous chemicals, producing compounds that perform as well as or better than existing ones and are biodegradable, avoiding auxiliary substances (such as solvents), reducing energy requirements, making use of renewable materials, and using catalysts in place of stoichiometric reagents are all important steps in developing sustainable chemical processes. (5) Chemical processes that, in addition to the desired result, generate significant amounts of byproducts and trash are less desirable.

It is possible that the careful design of chemical processes may result in a decrease in the amount of embodied energy, including physical, metabolic, and other forms of energy, as well as the environmental

repercussions of excessive energy use. In the pharmaceutical and agricultural industries, where bioactive compounds are often too delicate to tolerate the circumstances used in bulk chemistry, the need for selective transformations is at an all-time high. While performing a synthetic transformation, it is very necessary to investigate the potentially dangerous characteristics of all of the molecules that need to be synthesised, as well as the potentially dangerous attributes of all of the starting materials and reagents. In many processes that are used today, selective transformations that make use of catalytic processes help to decrease the amount of stoichiometric auxiliary chemicals that are required, which may, in the end, contribute to less waste being produced. In addition to this, they are able to carry out the key synthetic transformation in a way that is friendlier to the natural environment.

As worries about the environment and the economy have grown over the past several years, chemists are now required to search for as many catalytic reactions that are kind to the environment as is practically possible. In spite of the fact that the fundamental ideas behind different types of catalysis are similar to one another, the study of heterogeneous catalysis, homogeneous catalysis, and bio catalysis have developed into three separate scientific domains. This dispersion is the result of the various processes and research

techniques that are employed in the individual disciplines. These procedures and methodology give the bulk of the input for catalyst development and process design. Catalysis, which played such a significant role in the growth of industry in the 20th century, will also play a significant role in the development of the industry of the 21st century, which will be more environmentally friendly. Not only can catalysis help green chemical processes (for example, by substituting reagents or allowing for more efficient processes), but the demonstration of their worth will accelerate the greening of chemistry by minimizing the negative impact that processes have on the environment and reducing the costs associated with those effects. (6)

In the year 1835, the term "catalysis" was used to describe a circumstance in which the addition of a negligible amount of a foreign substance resulted in a considerable increase in the pace of a chemical reaction without the foreign material itself being consumed in the process. At that time, catalysis has been recognized as an intriguing phenomena, and there have been persistent efforts made to better understand it and find useful uses for it. This has led to the development of a number of technologies that, during this century, have enhanced the standard of living for humans. Catalysis is essential to the operation of almost all aspects of the chemical industry, and its contributions, whether direct or indirect, account for more than 20% of the gross domestic product of industrialized nations.

In many cases, the production of pharmaceuticals, pesticides, pigments, photosensitive chemicals, monomers, and other similar substances involves the utilization of a multi-stage chemical process that calls for the utilization of a wide variety of chemicals, catalysts, solvents, and other similar substances. It is crucial at this point for the compounds to interact with one another to the maximum degree feasible so that the reaction may be finished. On the other hand, these processes are often seen as being inherently incapable of being reversed. It is important to transport a moisture anion exchange reactant into an organic-soluble reactant or organic phase in order to circumvent the immiscibility problem. Some of the more conventional strategies (7) for overcoming this immiscibility include making use of protic and aprotic solvents, fast stirring rates, and high temperatures. These processes, on the other hand, are not without their share of drawbacks, including a significant consumption of energy, the production of by-products, difficulties in purification, and damage to the environment. Thus, these methods are not desired, they are insufficient, and they contribute to pollution on an industrial scale.

#### ➤ History of Phase Transfer Catalysis (PTCs):

Late in the 1960s, a practical method referred to today as "phase transfer catalysis" (PTC) (8) was developed to overcome the encounter issue produced by the mutual insolubility of aqueous and organic phases.

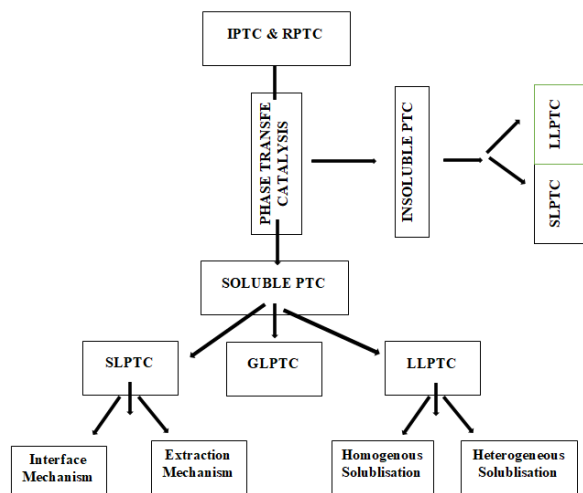
This key green method (9) that reduces waste utilizes water as a solvent and is applicable to a wide range of processes in which chemical & chemical metal ions, typically three to five, mix with organic substrates. Utilizing unequal two separate solutions, one component (water) is a storehouse of responsive anions or base for the creation of organic anions, while the second phase (organic) consists of sustainably cultivated reactants and catalysts. Combinations of lipophilic ions with lipophilic cations provided by the catalyst continuously release reactive anions into the organic phase. Starks et al. (8) proved that the immiscibility of a combination of sodium chloride cyanide and 1-chlorooctane prevents nucleophilic aliphatic substitution. Minutes after the addition of 1% hexadecyl tributyl phosphonium bromide, cyanide ions are transported into the organic phase, and 1-cyanoctane is produced quantitatively.

#### ➤ Steps involved in PTCs:

- 1) The stage in the transfer reaction in which the reactant anion is transferred from the aqueous or solid phase into the organic phase and the product anion is transferred from the organic phase into the aqueous or solid phase.
- 2) The phase of the reaction known as the intrinsic reaction, during which the product is generated in the organic phase. The optimization of each of these phases is dependent on a number of factors, the most important is the phase transfer catalyst's physical structure.

#### ➤ Variations of PTC Reactions:

Phase transfer catalysis (PTC) reactions may be categorized into two basic categories: soluble and insoluble (Figure 1). Within each class, reactions are further classified depending on the phases involved: liquid-liquid phase transition reactions (LLPTC), gas-liquid phase transition reactions (GLPTC), and solid-liquid phase transition reactions (SLPTRC) (SLPTC). This PTC is similar to classic insoluble PTC in which the complexation catalyst is immobilized on a solid substrate. In some instances, the phase transfer catalyst will produce its own unique liquid phase. Inverse PTC (IPTC) and reverse PTC (RPTC) are two more non-typical versions of PTC that use a reversed phase transfer mechanism.



**Figure 1: Types of PTC Reactions**

➤ **Selecting Phase Transfer Catalysts:**

The following are two conditions that are absolutely necessary for a PTC (17):

1. The phase transfer agent must be cationic and include sufficient organic structure to partition the nucleophilic anion into the organic phase. This is only possible if the agent has sufficient organic structure.
2. To ensure that there is a high amount of anionic reactivity, the cation-anion bond must be suitably loose.
3. When selecting a phase transfer catalyst, the stability of the catalyst under the reaction conditions, the ease of its separation or recovery, the convenience with which it can be made or acquired, its activity, and its toxicity are all relevant factors.

➤ **Applications of Polymer-Supported Phase Transfer Catalysts:**

Regan elucidated how the design of quaternary onium salts and the degree of ring replacement under triphase circumstances influence the displacement response of 1-bromooctane with aqueous sodium cyanide. There was no reaction seen in the absence of the catalyst. Cinquini et al. evaluated the effect of resins containing quaternary ammonium and phosphonium salts in a toluene/resin/water system in which 1-bromooctane was transformed into 1-iodooctane and octane carbonitrile. In displacement halides involving alkyl cyanide or another halide, phosphonium salts are more reactive than ammonium salts, according to the study. However, the pace of triphase reactions is slower than that of comparable transformations carried out in the presence of soluble PTC (25).

Ford et al. used polystyrene-bound benzyltributylphosphonium and benzyltrimethylammonium chloride in the displacement reactions of benzyl bromide, benzyl chloride, 1-bromooctane, and 1-

bromohexadecane with excess aqueous sodium cyanide. The reaction rates depended on stirring speed, catalyst particle size, percentage of cross-linking, and substrate structure. Under triphase circumstances, Tomoi et al. studied the effect of solvent on the intrinsic activity, ion exchange rate, and aggregation interaction of polymer-supported phosphonium ions.

In a three-phase reaction catalyzed by aqueous sodium hydroxide and polystyrene-bound benzyltrimethylammonium chloride, Balakrishnan et al. analysed the C-alkylation of phenylacetonitrile with 1-bromobutane. As a consequence of this research, the phrase "reverse addition" was coined to characterise a procedure in which the substrate to be alkylated was added to the reaction vessel first. The order in which the substrate was introduced to the catalyst had a significant effect on the rate of reaction. We investigated the kinetic data under the limitations of mass transfer and intraparticle diffusion. In addition, they have created a surface-enriched polymer-supported phase transfer catalyst and studied the kinetics of C-alkylation of phenylacetone and dichlorocarbene addition to various olefins under triphase conditions.

Murugan et al. have investigated the qualitative effects of catalyst type, aqueous-to-organic phase volume ratio, catalyst loading, and particle size under triphase catalyzed conditions. In a slurry reactor, phenol in alkaline solution and benzoyl chloride in toluene were reacted using a polymer-supported tri-n-butylphosphonium ion and a phase transfer accelerator. Using the fundamental theory of porous catalysts, the consequences of mass transfer have been investigated. Calculated inside the porous polymer particle are the reaction rate constant and diffusion coefficients. The stumbling block has been identified.

Wu et al. manufactured fine compounds utilising polymer-anchored ammonium salts in a triphase environment. The reaction of 4-methoxyphenylacetic acid with n-bromobutane in dichloromethane/alkaline solution using a triphase catalyst was also investigated.

Doraiswamy et al. investigated the kinetics of benzyl chloride esterification with aqueous sodium acetate by using polymer-supported tributylmethylammonium chloride as phase transfer catalysts. Compared to the kinetics of the reaction utilising soluble benzyltributylammonium chloride and soluble tributylmethylammonium chloride, the triphase catalyst is roughly fifty percent more reactive. Under solid–solid–liquid (SS-L) triphase conditions, polymer-supported aminopyridinium salts or tetra-phenylphosphonium chloride are also excellent catalysts for the fluorination of activated aromatic chlorides with solid, anhydrous KF, and may be reused without considerable loss of activity.

2,4-Dinitrochlorobenzene (DNCB) has been reported to have been fluorinated with solid KF in the presence of polymer-supported tetraphenylphosphonium chloride under solid–solid–liquid (S-S-L) phase transfer conditions. Triphase fluorination conformed to zero-order kinetics with respect to the DNCB concentration and first-order kinetics with respect to the catalyst concentration (29).

Polyacrylamide and its modified forms have been used as cosolvent-type catalysts for nucleophilic displacement reactions under biphasic and triphasic conditions, as supports for the solid-phase synthesis of peptides, for metal complexation, and for the preparation of a number of polymer-supported reagents. Tamami et al. described the use of quaternized amino-functionalized cross-linked polyacrylamide as a polymeric PTC in the synthesis of halohydrins and azidohydrins. Recently, they presented the discoveries that led to the successful creation of a simple and efficient method for the transformation of epoxides to -thiocyanohydrins using quaternized amino-functionalized cross-linked polyacrylamide as an efficient heterogeneous polymeric PTC (26).

#### ➤ Applications of PTCs:

PTC is used in a variety of chemical processes. In the presence of bases, its primary applications include nucleophilic substitution reactions and deprotonation of moderately and weakly acidic organic compounds. PTC-catalyzed reactions include oxidations, reductions, polymerizations, transition metal co-catalyzed reactions, synthesis of carbenes and further reactions of carbenes, addition reactions, condensations, etc., which are frequently performed in multi-step synthesis processes for the production of fine chemicals. Base-mediated alkylations of slightly acidic organic compounds. This removes the need for severe anhydrous conditions, expensive solvents, and dangerous bases like metal hydrides and organometallic reagents (27).

Instead of hazardous alkali metal alkoxides, amides, and hydrides, simple, affordable, and mild bases such as NaOH and K<sub>2</sub>CO<sub>3</sub> may be used in the presence of a phase transfer catalyst in biphasic systems. Makosza (9), for example, was a pioneer in the C-alkylation of active methylene compounds such as activated benzylic nitriles, activated hydrocarbons, and activated ketones under PTC/OH<sup>-</sup> conditions, which is widely used in a wide range of important chemical processes. According to Dehmlow, improved selectivity is an additional advantage of these reactions in some cases. During carbene reactions, phase separation precludes the hydrolysis of the organic substrate in the presence of 50% NaOH, for example. The need to separate the catalyst from the organic phase of the product is one of the most significant disadvantages of PTC, especially in commercial applications. Many general separation techniques are addressed in the conclusion. Another method for circumventing the challenges associated with catalyst recovery is to immobilize the PTC on a

stable platform. This is discussed in detail in the section on ultrasonography in PTC systems (28).

## CONCLUSION

Phase Transfer Catalysis (PTC) is an efficient method for the synthesis of organic reactions involving two immiscible-phased molecules, according to the present research. The objective of this study is to create a variety of soluble and insoluble phase-transfer catalysts for the heterogeneous synthesis of diverse chemical compounds using ultrasonic energy. While chemical reactants exist in immiscible phases, phase-transfer catalysts may carry one of the reactants over the interface into the other phase where the reaction occurs, resulting in fairly high conversion and selectivity. Generally speaking, quaternary onium salts, such as tetra alkyl ammonium or phosphonium salts (Q<sup>+</sup> X<sup>-</sup>), are efficient catalysts for speeding the growth of phase-transfer catalysis, a potential approach for organic synthesis. It calls for a straightforward experimental strategy, gentle reaction conditions, pricey and ecologically friendly materials and solvents, and has the potential for mass manufacturing. Nowadays, phase-transfer catalysis seems to be a prominent synthetic technique, valued not only in several areas of organic chemistry, but also in a wide range of industrial applications.

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