

What is the real mechanism of polymer-supported phase-transfer catalysis?

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Abstract - A comprehensive mechanism of the polymer-supported phase-transfer catalysis is suggested. The transport of organic reagent from the bulk phase through water to the catalyst particle is explained in terms of emulsion polymerization. The extraction equilibria are shown as a driving force for the change of surrounding solvents of active groups attached to the polymer. The oscillation of these groups between organic solvent and water phase inside the polymer particle is the basic condition of the reaction. Experimental data prove the theoretical considerations.

HISTORY AND SCOPE

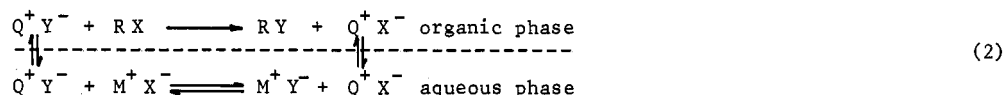
When in 1965 Makosza (ref. 1) described the alkylation of substituted phenols in presence of a quaternary ammonium base and called it a "catalytic two-phase reaction", he did not think that he was opening a new chapter of preparative organic chemistry. Quite independently, Brandstrom (ref. 2) in 1969 discovered a procedure for the synthesis of amine salts based on the "extraction of an ion pair" from an aqueous solution into methylene chloride or chloroform. The reaction proceeded also using such acids with which the traditional set-up consisting of anhydrous acid and amine fails. Later, he used the same approach for alkylation in a two-phase mixture. The last of the pioneers was Starks, who in 1971 introduced the term "phase-transfer catalysis" (ref. 3). He was also the first to recognize the great potential offered by the method and to define the mechanism of process which is still valid.

During several years, which followed after the publication of initial papers, the activity in the field increased considerably and the phase-transfer catalysis was described in numerous applications. In consequence, some reviews and monographs appeared (ref. 3-9).

The phase-transfer mechanism can be easily explained using a common nucleophilic displacement reaction as an example:



in which the nucleophile Y^- (in the aqueous solution) reacts with, e.g., alkyl halide RX (in organic phase) using an onium salt $Q^+ X^-$ as a catalyst:



In the aqueous phase, an ion pair $Q^+ Y^-$ is generated by a reaction between the salt of alkali metal $M^+ Y^-$ and the catalyst; due to the lipophilic character of Q^+ , the anion Y^- is extracted through the phase boundary into the organic phase. Here, the necessary contact with the alkyl halide is established, and displacement takes place. The displaced anion X^- is transferred back into the aqueous phase in the form of an ion pair $Q^+ X^-$, and the cycle is completed.

The mechanism outlined above shows that, in fact, the process is not catalysed by a quaternary salt. The misleading term "phase-transfer catalysis" was introduced because the original "catalyst" is recovered after the reaction is complete. Actually, the process consists in a controlled extraction of compounds from one phase into another. Therefore, it should be described in terms used in extraction. Unfortunately, the term phase-transfer catalysis has become so much popular that there is no sense of changing it.

Compared with the usual techniques of organic chemistry, the phase-transfer catalysis has a number of advantages which are summarized in Table 1.

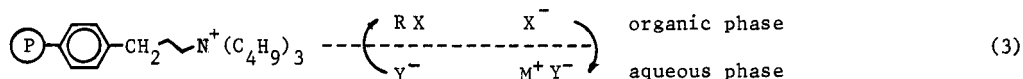
TABLE 1. Advantages of phase transfer catalysis over conventional procedures (ref. 8)

Expensive anhydrous or aprotic solvents not required
Improved reaction rates and/or lower reaction temperatures
Easier work-up
Aqueous alkali metal employed instead of alkoxides, amides, hydrides or metals
Occurrence of reactions that do not otherwise proceed
Modified selectivity
Modified products ratio
Increased yields through suppression of side reactions
Use of commercially available, inexpensive catalysts

All low-molecular weight compounds employed up to now as phase-transfer catalysts have one serious disadvantage: they have to be laboriously separated from the product after the reaction is finished. This can be overcome using insoluble catalyst. Thus, polymer-supported phase-transfer catalysts offer advantages common with heterogeneous catalysts (ref. 10,11): easy separation from the reaction mixture, recycling, use in a continuous flow reactor. The polymer-supported form has also disadvantages: physical attrition of particles, low chemical and thermal stability of polymer quaternary onium groups, lower activity, higher cost in comparison with soluble analogs, etc.

KINETICS AND MECHANISM OF POLYMER-SUPPORTED PHASE-TRANSFER CATALYSIS

Although the mechanism of phase-transfer catalysis using a polymer-supported catalyst has been described in a number of papers (ref. 11-19, 21, 47), the mechanism has not been cleared up enough. So far, a few different approaches to the explanation of the role of a polymer-supported catalyst have been reported (ref. 11, 21, 47), in which not all the essential differences between soluble and insoluble catalysts are considered. While, e.g., migration of ion pairs between both phases is free when a soluble catalyst is used, in the case of insoluble catalysts the free migration is excluded because the cation is part of the solid polymer. Most of the authors do not assume any difference between the reaction mechanism using low-molecular weight catalysts and polymer ones (ref. 20). In fact, it cannot be neglected that the phase boundary, through which the complete ion pairs $Q^+ Y^-$, or the anions Y^- only are transported, is an area in the two-phase system. However, in the three-phase system this suggestion fails. The original flat boundary changes to a very small volume which includes the catalytically active group and both liquid phases. This space should be situated closely to the bound cation near to the polymer chain. If the polymer salt is to be active, it has either to be just on the boundary of the two phases or to fluctuate between them:



Another view (ref. 21) consists in an assumption of the aggregation of polymeric quaternary onium ions in water containing domains resembling inverted micelles.

TRANSPORT OF ORGANIC COMPOUNDS TO THE POLYMER PARTICLE

The three-phase system consists of an aqueous salt solution, serving the dispersion medium, in which solid polymer particles and small droplets of the solution of an organic reagent in water-immiscible solvent are dispersed. The aqueous solution is not only a dispersion medium. It swells the polymer particles and forms also an unstirred liquid film on the outer surface of both the polymer particles and the droplets of organic solution. The transport of water-soluble ions into the polymer through water obeys rules valid for ion exchange which have been known for a long time (ref. 45). In this case, the role played by stirring is decisive not only with respect to the maintenance of a homogeneous concentration of the aqueous phase. With increasing rate of stirring, the thickness of the adhering film decreases (ref. 46). Experimental data indicate that the increase of the stirring rate has a positive effect on reaction rate within limits (ref. 12, 13, 22-25) (Fig. 1). Diffusion through the film is not the rate-determining step. This is also confirmed by the generally described dependence of the reaction rate on the concentration of functional groups in the polymer catalyst (ref. 21, 23, 24, 26-30). This conception is also described in literature (ref. 11, 12).

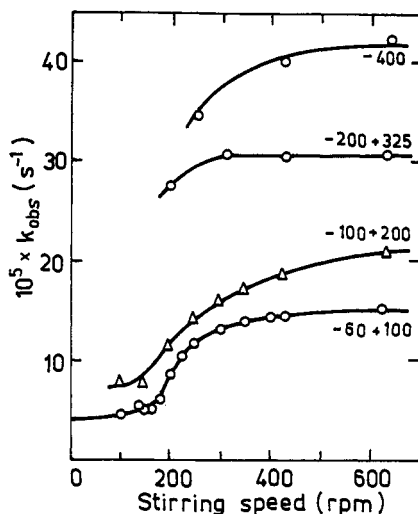


Fig. 1. Dependence of observed reaction rate constant, k_{obs} , on stirring speed and particle size (mesh) of 2% crosslinked polystyrene catalyst with (tributylammonio)methyl groups (17% ring substitution) for reaction of bromooctane in toluene with 10 molar equiv. of sodium cyanide and 0.02 molar equiv. of catalyst at 90°C (ref. 19).

So far, however, nobody has queried the problem how the organic solvent, and especially the reagent dissolved in it, reaches the polymer domain. A faint conception assuming contacts between polymer particles and organic droplets (ref. 12) or the newly proposed alternating shell model (ref. 47) contradict the presence of the quiet layer (film) of the aqueous phase surrounding both dispersed species as mentioned above. Having in mind the scheme representing the three-phase system (Fig. 2), we cannot miss an extraordinary analogy between polymer-supported phase-transfer catalysis and emulsion polymerization (Fig. 3). The latter also proceeds with the formation of a three-phase system containing droplets of the still unpolymerized monomer (analogous to organic phase), water solution of initiator (aqueous phase), and stabilized polymer particles swollen with the monomer (polymer-supported catalyst). Radicals $I\cdot$ penetrate into the particle directly from the water phase. The organic compound is transported through the aqueous phase as well. One part of it is dissolved in water from which the polymer enters. This transport mechanism can also be entirely adopted for the polymer-supported phase-transfer catalysis. Of course, it is somewhat more complicated. The dispersed organic phase of two components (solvent and reagent) resembles the dispersed phase known from emulsion copolymerization. However, only one of the compounds is

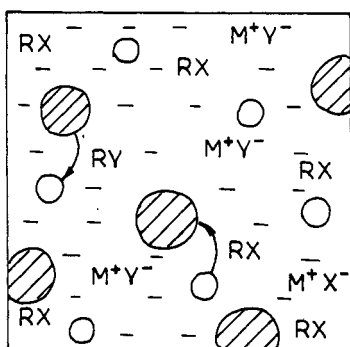


Fig. 2

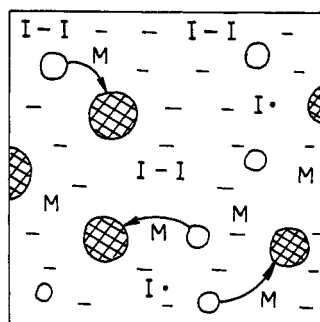


Fig. 3

Fig. 2. Schematic picture of a three-phase system where a polymer-supported phase-transfer catalysis takes place. Open circles relate to droplets of organic phase, hatched circles relate to solid polymer catalyst, RX, RY, M^+X^- , and M^+Y^- , represent species dissolved in water.

Fig. 3. Schematic picture of a system where emulsion polymerization takes place. Open circles are for stabilized monomer droplets, cross-hatched circles relate to growing polymer particles, M, I-I, and $I\cdot$ relate to monomer, initiator, and free radicals dissolved in water, respectively.

TABLE 2. Imbided solvent composition under triphase conditions

Catalyst	Crosslinking agent	Quaternary	Water	Water + Toluene	Toluene	Ref.
		ammonium groups	g/g			
	%	mmol/g				
G-60	40	0	1.62	1.41 + 0.26	1.64	44
G-60-N ⁺ Bu ₃	40	0.30	1.37	1.29 + 0.08	1.14	44
G-60-N ⁺ Bu ₃	40	0.97	1.43	1.24 + 0.12	1.03	44
G-97.5	2.5	0	0.80	0.68 + 0.17	0.07	44
G-97.5-N ⁺ Bu ₃	2.5	1.52	1.60	1.14 + 0.10	0.46	44
S-99-N ⁺ Bu ₃	1	1.10	0.18	0.81 + 0.57	0.62	21
S-99-N ⁺ Bu ₃	1	2.01	12.49	11.91 + 0.43	0.35	21

G = copolymer glycidyl methacrylate - ethylene dimethacrylate

S = copolymer styrene - divinylbenzene, the number denotes the amount of monovinyl compound in the polymerization feed

active. Moreover, after the chemical reaction in the catalyst particle is completed, the products (the new organic compound and displaced ion) have to diffuse back into the bulk medium. Hence, neglecting water and organic solvent, we deal with the transport of four species: two into the particle and another two out of it. Water and the organic solvent are contained in the polymer already since its equilibration before the reaction starts. Usually, the organic phase is added later on. From the thermodynamic point of view, the way in which the equilibrium is reached, and thus also the order in which the phases are feeded is not decisive. At the moment, when the organic phase is mixed with water, it dissolves to a very dilute true solution (e.g., 0.05 wt.% of toluene in water at 25°C). But even the low concentration is sufficient to mediate transport to the polymer domain. The thermodynamic equilibrium is established after some time and the flux of the solvent ceases. Now, the polymer contains both water and organic phase in equilibrium amounts. This can be readily simulated by stirring of polymer particles in a water-solvent mixture, followed by measurement of the content of both phases in the polymer (Table 2).

The content of organic phase depends on the hydrophilicity of the catalyst, which is a function of a concentration of attached quaternary ammonium groups and of the length of alkyl substituents. Even though molecules of both water and solvent migrate in and out of the polymer, as has been proved by ¹³C NMR (ref. 31), their total equilibrium amounts in the polymer remain constant.

A theoretical model developed by Morton (ref. 32) expresses the equilibrium volume fraction of polymer, v_2 , in the swollen particles, when placed in contact with an aqueous medium where the organic solvent is immiscible. Thus, Eq. 4 gives the Flory-Huggins partial molar Gibbs free energy $\Delta\bar{G}_1$, and the interfacial contribution, $\Delta\bar{G}_{1,i}$, from the Laplace equation, since the particles attain a certain radius r_p at equilibrium

$$\Delta\bar{G}_{1p} = \Delta\bar{G}_1 + \Delta\bar{G}_{1,i} = RT [\ln(1 - v_2) + (1 - 1/x) v_2 + \chi v_2^2] + 2V_1 \gamma / r_p = 0 \quad (4)$$

Here, V_1 is the molar volume of the solvent, γ is the interfacial tension between the solvent and water, and χ is the Flory solvent-polymer interaction parameter which is dependent on temperature T . Finally, the normalized volume correction, of the polymer segment with respect to the size of the solvent $x = v \bar{M}_n / V_1$ where v is the specific volume and \bar{M}_n is the number-average molecular weight of the polymer. Eq. 4 holds for equilibrium. With respect to the kinetics of any reaction, it is important to know how fast the equilibrium is reached. The rate of swelling, which substitutes the rate of transport of a reagent to the surface of the particle, with which it interacts in phase-transfer catalysis, is described in equation 5 (ref. 33):

$$\frac{dV_{1p}}{dt} = \frac{4\pi r_p N_p r_o N_o D_w c_{o\infty}}{r_p N_p + r_o N_o} \left[\exp\left(\frac{2V_1}{r_o}\right) - \exp\left(\frac{\Delta\bar{G}_{1p}}{RT}\right) \right] \quad (5)$$

where V_{1p} is the volume of the organic compound in the polymer, r_o and r_p are the radii of droplets of the organic phase and polymer particles, respectively, N_o and N_p are their respective numbers, D_w is the diffusion coefficient of the organic compound in water, and $c_{o\infty}$ is the concentration of the organic compound in water when dissolved from a planar surface. In the case $r_p N_p \gg r_o N_o$, which is usually fulfilled when a moderate excess of organic phase is applied and therefore it is close to phase-transfer catalysis, Eq. 5 may be simplified to (ref. 34):

$$\frac{dV_{1p}}{dt} = 4\pi r_o N_o D_w c_{o\infty} \left[1 - \exp\left(\frac{G_{1p}}{RT}\right) \right] \quad (6)$$

Since $r_o N_o = 3V_o/4\pi r_o^2$, where V_o is the total volume of the organic phase,

$$\frac{dV_{1p}}{dt} = \frac{3V_o}{r_o^2} D_w c_{o\infty} \left[1 - \exp\left(\frac{\Delta\bar{G}_{1p}}{RT}\right) \right] \quad (7)$$

Eq. 7 shows that the rate at which the organic liquid transported through the aqueous medium enters the polymer is inversely proportional to the square of the droplet radius. The concentration of the organic phase in water also depends on both of these variables. According to the Higuchi-Misra rule, the solubility of a slightly soluble organic liquid in water, c_{or} , is given by

$$c_{or} = c_{o\infty} \exp(2V_1/r_o RT) = c_{o\infty} \exp(K/r_o) \quad (8)$$

The higher the droplet radius, the lower the concentration of the organic compound in water. Eq. 8 holds for one component organic liquid only, but it can be extended for a multicomponent mixture, thus simulating the phase-transfer catalysis even more exactly.

Stirring affects not only the thickness of the adhering surface film, but also the transport rate of organic compounds into the polymer domain. The transport of the organic reagent is not the rate-determining step in the case of stirring intensity which corresponds to the plateau in curves shown in Fig. 1. Why the apparent reaction rate is independent of stirring, when the certain limit (usually 500-800 rpm) is exceeded? The reason consists in the fact that after a minimal size of droplets, and thus a sufficient concentration of reagents is reached, a process different than the transport through the bulk solution becomes operative. This process may be either diffusion inside the polymer particle, or processes related to the transfer between phases, or the chemical reaction itself.

TRANSPORT OF COMPOUNDS INSIDE POLYMER PARTICLE

Diffusion inside a polymer particle generally obeys Fick's law, and the flow rate of the compound is proportional to the concentration gradient. If the reaction proceeds inside a particle, the concentration of the reacting compound steadily drops below the thermodynamical equilibrium value. The system tries to supplement the reacted amount from the bulk solution, and reagents flow into the particle due to the gradient formed. As a result, however, reaction products, having a higher concentration compared with the bulk solution, accumulate in the catalyst particle and diffuse from it to the surrounding medium owing to its gradient. While the released inorganic ions remain in the aqueous solution, the organic product is transported back to the bulk organic phase according to the mechanism described for the mass transfer from the droplet to the particle.

Leaving an investigation of the detailed course of the chemical reaction itself out of consideration, we have to describe the diffusion and chemical reaction in the porous "catalyst" jointly. The problem, which is common in technologies using heterogeneous catalysts, has been described theoretically already at the end of the thirties. An analysis of the effect of mass transfer within a porous structure on observed reaction characteristics has resulted in a quantitative description of variables which determine the effectiveness factor of the porous catalyst. The factor η is defined as the ratio of the actual reaction rate to that which would occur if all of the surface throughout the inside of the catalyst particle were exposed to a reactant of the same concentration and temperature as that existing at the outside of the particle (ref. 35). For the irreversible first-order reaction and spherical shape of the catalyst we have

$$\eta = \frac{3}{\phi_s} \frac{1}{\tanh \phi_s} - \frac{1}{\phi_s} \quad (9)$$

where ϕ_s is defined as a dimensionless quantity, termed the Thiele modulus

$$\phi_s = r_p k'/D_{ef} \quad (10)$$

Here, k' is the intrinsic reaction rate constant per unit of gross volume of catalyst particles, $D_{ef} = DH/\tau$, D is the diffusion coefficient in the water phase outside the particle, H is porosity and τ is an empirical factor (tortuosity). Eq. 9 has an important practical implication. The effectiveness of a catalyst becomes small for large particles, a high rate constant or small values of D_{ef} . Unfortunately, very active catalysts tend to have low effectiveness factors, and, actually, the reaction proceeds only close to the surface of the particle while the groups buried inside remain unemployed. Hence, there is no reason to improve only one characteristic property of the catalyst in order to reach high activity. On the contrary, only an optimal combination may be successful.

DISTRIBUTION OF REAGENTS

Now, it should be elucidated in which form the organic phase is present in the polymer. As shown in Table 2, the amount of the organic solvent in the polymer is certainly higher compared with its solution in water. The solvent solvates polymer chains which have a relatively low polarity. In fact, the amount of the reagent in the polymer and its diffusion rate inside the particle are decisive; this does not apply to the amount of the imbibed solvent, e.g., toluene.

In the system bromooctane-toluene-catalyst, the concentration of the reagent in the polymer, which is in contact with the external bulk solution, is proportional to the distribution coefficient. If the amount of imbibed toluene in the polymer catalyst, composition of the bulk solution and the distribution coefficient are known, it is possible to calculate the concentration of the reagent (Table 3). This concentration alone plays the major role in the rate of chemical reaction. As shown in the Table 3, the amount of bromooctane localized in the polymer is 2-4 times higher than in the bulk solution used. It is a consequence of interactions between bromooctane and polymer chains, characterized by the Flory parameter χ . Obviously, the reagent is present in the polymer to a small extent as a true aqueous solution, but mainly as part of organic liquid mixture which solvates hydrophobic polymer chains.

TABLE 3. Preferential sorption of bromooctane on modified glycidyl methacrylate - ethylene dimethacrylate beads

Catalyst	Crosslinking agent %	Quaternary ammonium groups, mmol/g	Bromooctane in resin, g/g	
			calculated ^a	found ^b
G-60-N ⁺ Bu ₃	40	0.97	0.18	0.39
G-97.5-N ⁺ Bu ₃	2.5	1.52	0.07	0.22

^aCalculated from the amount of imbibed toluene assuming no preferential sorption. Initial concentration of bromooctane in toluene is 0.188 g/mL.

^bMeasured by GLC

Solvation of chains may exert a positive effect on the diffusion rate within the polymer particle. If the distance which has to be overcome by the molecule of the reagent in the aqueous solution inside the particle is rather long, which is the case of macroporous supports, the diffusion slows down the process, the overall transport of reagent decreases, and the macroporous catalyst seems to be less active than catalysts based on gel-like supports.

The above discussion explained the penetration of reacting components from the bulk phase into the polymer. Coexistence of the two phases has necessarily to be achieved in this case. But this is not enough. Both phases have to communicate with the corresponding phases (solutions), which are part of the bulk phase, because this is the condition of supply of reagents to the reaction sites and of the removal of reaction products from the polymer in which they cannot accumulate. In other words, some sort of communication has to exist between the externally situated phase and each reactive group inside the catalyst which is to be active. Hence, a mechanism assuming formation of separated "pools" of water resembling inverse micelles (ref. 21) may be ruled out. Moreover, the micellar mechanism of the phase-transfer catalysis was refused by Starks (ref. 36) as early as 1973.

THE 'CATALYSIS'

The previously described pathway brought the reagents close to the active site of the polymer. Now, our attention should be paid to the reaction itself. Basically, there is no reason why the sequence of reaction steps shown in Eq. 2 should have a different character in the polymer-supported version. This is also assumed, tacitly or explicitly (e.g., ref. 48), in the majority of papers. Here, too, the decisive step for the course of the chemical reaction itself is the transfer of the anion from one phase into another. Moreover, Montanari's experiments with alkylation of naphthoxide proved that the alkylation takes place exclusively in the organic phase (ref. 48). On the other hand, it has been reported (ref. 46) that the ion exchange runs in an aqueous medium only, because salts do not ionize in nonpolar solvents. Hence, to start the reaction, the inactive counterion (anion) has to be exchanged for another, a reactive one. Since the reactive anions are present in the water phase only, the exchange has to occur there, and the cation bound to the polymer has to be in contact with this phase. It has been mentioned, however, that the nucleophilic displacement itself proceeds in the organic phase. Consequently, to facilitate such reaction, the ion pair (polymer-supported cation + reactive anion) has to change the surrounding medium. In order to continue, the pair has to oscillate between the aqueous and organic phase.

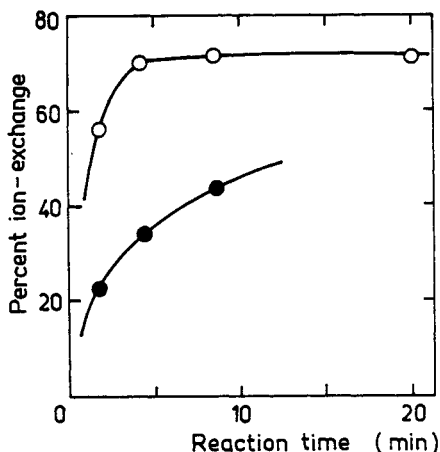


Fig. 4. Dependence of ion-exchange rate for 2% crosslinked polystyrene catalyst with (tributylammonio)methyl bromide groups on percentage of ring substitution (open circles 9%, full circles 36%). Sodium acetate 0.08 mol, water 26 ml, toluene 20 mL, particle size 74-149 μm , temperature 30°C, stirring rate 650-700 rpm (ref. 42).

There are two extreme ways for such a process: both liquid phases move, or the attached active groups switch one medium to the other due to the conformational motion of the polymer chain. The concept of changes of liquid phases is favoured by the fact that a catalytic activity is also observed with catalysts supported on carriers in which the mobility of chains can hardly be assumed, e.g., on silica (ref. 46). The other possibility is corroborated by an enhanced activity of groups bound to the solid support via spacer which up to a certain length extends the "radius of action" and accelerates the mobility of the immobilized ion pair (ref. 22, 24, 26, 30, 37-39).

Tomoi suggested fluctuations of the ion pair when studying the rate of ion exchange (ref. 26, 42), which is much slower compared with water alone under conditions of phase-transfer catalysis (Fig. 4). In this case the ion exchange takes place in water only, in which, however, not all groups are permanently situated. Thus, the total exchange occurs only after the time required by all groups to pass through the aqueous phase by interphase fluctuations.

From the above discussion we can see that both processes, i.e., exchange of liquids and chains motions, may participate in the oscillation. A question arises, what is the driving force causing these changes? We would remember what was said at the very beginning: the phase-transfer catalysis in general, and therefore the polymer-supported one too, is not catalysis but extraction. The extraction equilibria are well described since a long time ago (ref. 8). The transfer of, e.g., anion X^- along with the cation Q^+ from one medium into another is described by the stoichiometric extraction constant $E_{Q^+ X^-}$.

$$E_{Q^+ X^-} = \frac{[Q^+ X^-]_{\text{org}}}{[Q^+]_{\text{aq}} [X^-]_{\text{aq}}}, \quad (8)$$

which has a similar form also for the pair $Q^+ Y^-$. It is just the difference between the extraction constants that is the driving force of ion motions in the phase-transfer catalysis. The differences in the values involved are not insignificant, but amount to one order of magnitude or more. E.g., tetrabutylammonium salts in the mixture methylene chloride-water have $E_{Q^+ Cl^-} = 0.35$, while $E_{Q^+ Br^-} = 17$, i.e., approximately 50 times more. Extraction processes are responsible that the onium salt with the bromide anion would tend to be surrounded by an organic solvent in which the reaction proceeds, while with respect to the $E_{Q^+ Cl^-}$, the chloride form favours the aqueous medium, and hence also ionization. Consequently, extraction is the driving force which ensures changes in the solvent surrounding the "catalytically" active ion pair bound to polymer carrier. The main effect in the traditional phase-transfer catalysis is exerted by lipophilicity of the cation, nature of anion, and type of organic solvent. Numerous studies have proved that also in the polymer-supported version of phase-transfer catalysis these effects play an important role (ref. 12-14, 28, 40, 41). But the effects are more complex. Thus, e.g., the organic solvent affects not only the transport rate, but also the extent of swelling of the polymer particles, and thus the accessibility of active groups localized inside.

EXPERIMENTAL RESULTS

In the description of polymer-supported phase-transfer catalysis, performed within a theoretical analysis of the mechanism, the efficiency of stirring (thickness of film, solubility of the organic phase in water), particle size, diffusion coefficients of reactants in the polymer matrix, extraction equilibria, etc., were expressed. In fact a huge number of parameters should be considered. Let us examine one of the variables in detail. There is no author who

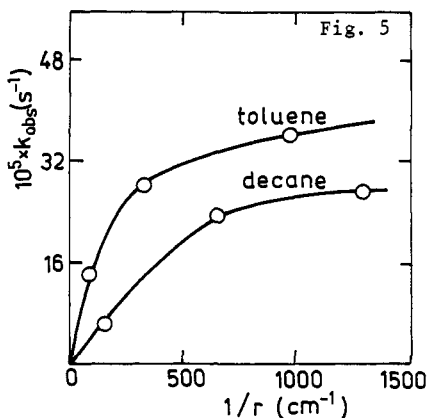


Fig. 5. Dependence of observed reaction rate constant, k_{obs} , on mean particle size and organic solvent for reaction of bromooctane with 10 mol-equiv. of sodium cyanide in water and 0.02 mol-equiv. of 2% cross-linked polystyrene catalyst with (tributylammonio)methyl groups (17% ring substitution). Stirring rate 600–650 rpm, temperature 90°C (ref. 12).

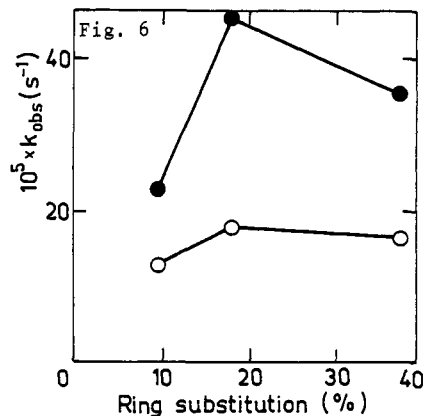


Fig. 6. Dependence of observed reaction rate constant, k_{obs} , on percentage of ring substitution for reaction of bromooctane with 10 mol-equiv. of sodium cyanide in water and 0.02 mol-equiv. of 2% (full circles) or 10% (open circles) crosslinked polystyrene catalyst with (tributylammonio)-methyl groups. Stirring rate 600–650 rpm, particle size 75–125 μm , temperature 90°C (ref. 22).

has not recorded a relationship between the particle size of the catalyst and the reaction rate (e.g., ref. 12, 13, 15, 17, 24, 25, 43, 44) (Fig. 5). In general, the dependence is linear within a wide range of diameters. Thus, e.g., a macroporous catalyst of the methacrylate type with a particle diameter of 30 μm has an activity in the reaction of bromooctane with potassium cyanide by 50% higher compared with the particle size 200 μm (ref. 44). In the same reaction catalysed by the gel-type modified styrene-divinylbenzene copolymer the slope of dependency between the reaction rate and particle size begins to be zero (it means the diffusion is not the rate-controlling step any more) with the particle size 20 μm (ref. 12). The particle size, at which transition from the diffusional to the kinetic region occurs, depends also on the reaction rate of the chemical reaction itself (cf. Eq. 10). In contrast to the reaction of bromooctane, a 400 fold acceleration was monitored with benzyl bromide using particles with the diameter 0.27 μm instead of 25 μm (ref. 17). Since most of the authors do not use particles of micron or even submicron size, because they are not readily available and are not easy to manipulate, in the majority of studies, particles having diameters of hundreds μm were used. In that case, only groups localized close to the particle surface are catalytically active. The dependence of the reaction rate on the content of active groups which is often reported (ref. 21, 22, 24, 26–30, 44) (Fig. 6) is in good agreement with this statement. Even if the homogeneous substitution of particles is assumed, concentration in the surface layer increases with the increasing total substitution. The higher the number of groups available, the larger the number of anions transferred from one phase to the other within a time unit, and the higher the observed reaction rate. Nevertheless, if the reaction rate itself is sufficiently high and the intraparticle diffusion flow (rate-determining step) remains unchanged, the thickness of the layer, in which the reaction takes place, decreases with increasing substitution, and no positive effect can be achieved. Moreover, substitution also brings about changes in swelling, in both water and the organic solvent.

An alternative to the use of independent submicron particles may take advantage of the special morphology of macroporous polymers which are composed of a three-dimensional array of very small "globules" with individual diameters of approximately 0.1 μm separated from one another by large void spaces or "macropores". When compared to gel polymers, the macropores may actually help facilitate diffusion of the liquid phase to the individual globules where the reactive centers are located. Diffusion through the bulk of an individual globule is somewhat similar to diffusion through a gel polymer bead with the same degree of crosslinking (ref. 14), though the distance to be covered within the individual particle is much shorter in the case of an individual globule located within a macroporous bead. Indeed, the major part of the transport takes place in the macropores and might therefore be facilitated. In fact, it is this property of enhanced diffusion which provided much of the drive for the development of macroporous resins (ref. 14, 22). Yet actual rate measurements for model reactions have consistently shown that in the case of macroporous resins reactions proceed slower than with gel polymers containing the same percentage of crosslinking.

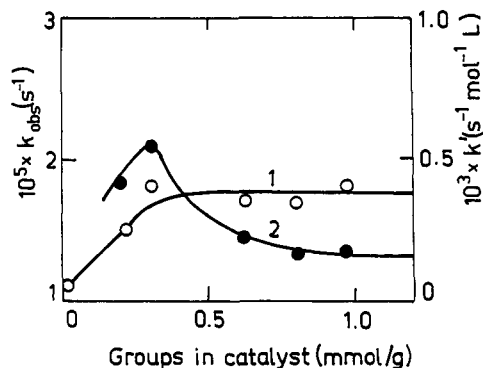


Fig. 7

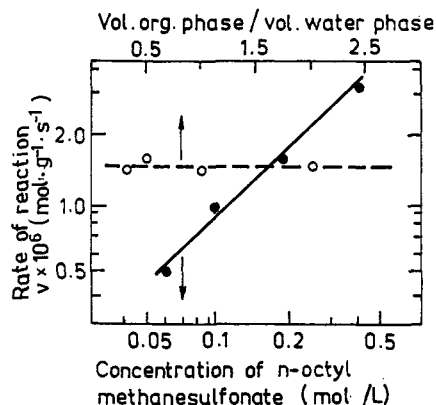


Fig. 8

Fig. 7. Effect of functionalization of macroporous 40% crosslinked glycidyl methacrylate catalyst with alkyltributylammonium groups on the observed reaction rate constants, k_{obs} (open circles) and normalized rate constant, k' (full circles) for reaction of bromooctane (0.14 mL) in toluene (0.8 mL) with sodium cyanide (0.392 g) in water (1.2 mL). Stirring rate 560 rpm, temperature 90°C (ref. 44).

Fig. 8. Dependence of observed rate of reaction, v , of octyl methanesulfonate with potassium bromide on the volume ratio of organic to water phase at concentration of sulfonate in toluene 0.2 mol/L (upper curve) and on concentration of organic reagent in toluene at concentration of bromide in water phase 4 mol/L (lower curve) catalyzed by 1% crosslinked polystyrene catalyst with (tributylammonio)methyl groups (0.95 mmol/g). Stirring rate 600 rpm, particle size 36–75 μm , temperature 85°C (ref. 25).

A possible explanation for this phenomenon which is observed for styrene-divinylbenzene resins is that the lipophilic character of the pores favors their penetration and filling by the organic phase with concomitant exclusion of aqueous phase (ref. 14); if this were indeed the case, then a solution to this problem would be to design and use more hydrophilic polymer matrices. Copolymer glycidyl methacrylate-ethylene dimethacrylate modified to incorporate quaternary ammonium groups can safely be considered to be more hydrophilic than similarly crosslinked styrene resins.

Figure 7 shows the effect of the capacity of the methacrylate macroporous resin on the rate constant k_{obs} and k' recalculated for a uniform 1 mole of active groups in the catalyst. Curve 1 which plots the change in k_{obs} with the capacity is of particular interest as it shows an initial rate increase until a maximum is reached when the concentration of active groups reaches approximately 0.3 mmol/g. A further increase in capacity does not result in a further acceleration of the reaction, in fact, the recalculated rate constant k' is seen to decrease. Such behaviour clearly suggests that not all functionalized sites possess equal reactivity and it can safely be speculated that most active sites are those which are exposed on the surface of the globules or even only on the surface of beads themselves. In contrast, the groups located within the globules or particles are essentially unreactive due to the restricted diffusion within the polymer mass. The resulting activity of macroporous polymer with higher hydrophilicity is not improved in comparison to the styrene-based resins and it is far from the activities of gel polymers.

An investigation of the reaction of modified macroporous glycidyl methacrylate particles containing primary amino groups (precursor of quaternary ammonium groups) with the dansyl chloride under conditions similar to phase-transfer catalysis proved that only surface groups are really active. SEM micrographs of the cross-section of a reacted particle clearly show that the reaction occurs really in the surface layer only, irrespective of porosity.

It is known, that these sorbents with amino groups are able to adsorb copper(II) ions from aqueous solution (ref. 49). The complexation reaction can be a good tool for the detection of accessibility of amino groups in the polymer particle. The microprobe examination of the cross-section of a particle shows again the same picture. Only the surface groups are active.

Most of the published papers describe experiments under conditions in which the stirring is effective enough not to affect the reaction rate. At the same time, the rate predominantly depends on the particle size. It is evident that under usual conditions, diffusion through the particle is the rate-controlling step. So far, it cannot be decided which of the two reacting species diffuses slowly. Most probably, the organic one. To increase considerably

the reaction rate of polymer-supported phase-transfer catalysis, a procedure has to be found which would increase the amount of organic reagent transported into the polymer domain. This may be achieved up to a certain limit given by the solubility, e.g., by raising the gradient, i.e., by a higher concentration of the reagent in the organic phase. The dependence reported by Takeuchi et al. (ref. 25) is steep (Fig. 8). At the same time, a mere increase in the volume of organic phase, which in fact also causes a rise in the total reagent concentration in the system is completely inefficient (Fig. 8). Another possibility is the search for more suitably organic solvents and the use of particles of micron size or completely new supports (ref. 50). The theoretical considerations and some experimental results reported here seem to offer a sufficient proof that the reaction rate can be increased using the polymer-supported phase-transfer catalysis, and that polymer catalysts may become competitive, compared with low-molecular weight ones.

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