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ION EXCHANGE CATALYSIS AND MATRIX EFFECTS

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I. INTRODUCTION

Ion exchange catalysis involves the use of ion exchange resins to promote reactions normally catalyzed by mineral acids and bases. The resins typically employed are sulfonic acid cation exchangers in the hydrogen form or quaternary ammonium anion exchangers in the hydroxide form. The chemistry of the acidic or basic moieties bound to the polymeric matrix, most commonly polystyrene crosslinked with divinylbenzene (see Figure 1), is essentially unchanged from that exhibited by free mineral acids and bases in homogeneous catalysis. Thus, ion exchange catalysis offers a means to achieve the equivalent of acid or base catalysis with a material which is particulate and therefore easily separated from the product by mechanical means. A number of processing advantages result. Perhaps even more important, ion exchange catalysis can produce chemical results difficult or, in some cases, impossible to achieve by homogeneous acid/base catalysis. These benefits occur because the polymeric matrix forming the skeleton of the resin bead introduces physical effects which can profoundly influence the course of the reaction. This bulletin describes the origin of these effects and suggests means to employ them so that the chemical and physical advantages available by resin catalysis might be realized.

Resins appear to be heterogeneous catalysts, but the classification quasi-homogeneous is more fitting since the catalysts perform their function by chemical reactions akin to those produced by dissolved acids and bases. Ion exchange resins are the acid/base counterparts of the new class of heterogenized homogeneous catalysts described by Pittman (29), Bailar (3), and Hanson (15), which are prepared by chemically anchoring a known metallo-organic homogeneous catalyst to a polymeric matrix. In this heterogenized form, the catalysts can be employed in place of their homogeneous counterparts and the valuable catalytic species easily recovered by mechanical separation.

Heinemann (18) has suggested the existence of orientation parameters in resin-bound catalysis similar to those known to apply in enzymatic catalysis. He predicts a trend toward unification of homogeneous and heterogeneous catalysis as proof accumulates which demonstrates the close relationship of the active intermediates in both types of catalysis. Evidence has already accumulated indicating ion exchange catalysts satisfy many qualifying criteria. A study of the chemical and physical phenomena involved in ion exchange catalysis will prove useful to the investigator interested in any area of polymer-bound catalysis. Observations are already being cited to the effect that in their heterogenized form, some heterogenized homogeneous metallo-organic polymers are better catalysts than in their free form (10, 14), suggesting that the matrix enhancement observed in ion exchange catalysis is also operative in the area of polymer-bound metal catalysis.

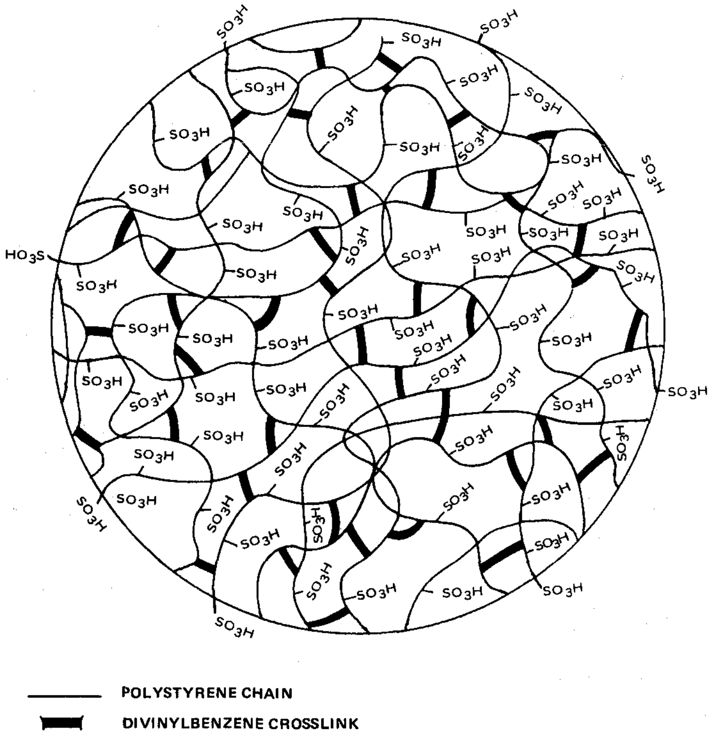

Figure 1. Pictorial representation of sulfonic acid cation exchange resin.

II. RESIN STRUCTURE AND ITS CATALYTIC CONSEQUENCES

Section VIII lists a number of different AMBERLITE®and AMBERLYST®ion exchange resins suitable for catalytic applications. All of the resins listed are composed of long chains of polystyrene locked together by means of divinylbenzene crosslinks into a three dimensional, insoluble polymeric phase called the matrix (Figure 1). The various resins differ in divinylbenzene content and in the concentration of acid or base moieties per unit volume. These are differences of degree and offer the experimenter flexibility in choosing a suitable catalyst for any reaction performed in a solvent which swells the resin matrix. The resins can also be divided into two groups having major structural differences, gelular and macroreticular resins. This structural difference has catalytic significance great enough to expand applications with macroreticular resins into areas not possible with gelular resins, such as reactions in non-swelling solvents. The nature and consequences of these differences will be discussed below.

Gelular Ion Exchange Catalysts

Application of the name gelular to describe this general class of ion exchange resins is somewhat misleading. Although the name may bring to mind an amorphous, distortable, jelly-like material; in fact, gelular resins are rigid transparent spherical beads, as shown in Figure 2. On a microscopic scale, the three dimensional polymeric gelular matrix is a homogeneous structure with no discontinuities. Acid catalysts have sulfonic acid ($-SO_3H$) groups bonded to the matrix, and base catalysts, tetralkylammonium hydroxide groups ($-NR_3OH$). If gelular beads are totally dry, the polymeric matrix is collapsed and the polystyrene chains are as close as atomic forces will allow. In this condition, the matrix is completely impervious to any molecule incapable of acting as a swelling medium. Thus, unless a reactant is itself capable of swelling the matrix, the collapsed gelular bead would exhibit almost no catalytic activity because only the relatively few catalytic sites on the bead's surface would be available to the reactant, and their number is insignificant compared to the total number contained within the body of the bead. Catalysis by gelular resins, therefore, requires the use of a swelling medium capable of expanding the polymeric matrix sufficiently so that solvent-filled spaces are created between the long polystyrene backbone chains of the matrix. These spaces constitute the microporous structure of the gelular phase and they are the means by which the reactant enters the body of the bead and is permitted to move within the bead. Such movement, called diffusion, is a necessary requirement to achieve a high degree of reactant/catalyst contact (20, 24).

Gelular resins are characterized by divinylbenzene contents below 12 percent. At crosslinker levels above 12 percent, the matrix exhibits great resistance to swelling. Diffusivity and associated exchange kinetics are very unfavorable, so that highly crosslinked gelular resins are very poor catalysts.

Macroreticular Ion Exchange Catalysts

The necessity for matrix expansion has been a limiting factor in the application of gelular catalysis, since it meant no appreciable catalytic activity would be evidenced in non-swelling solvents. This limitation was removed with the introduction in the 60's of a class of resins with a new type of structure (23, 25). Whereas gelular beads are homogeneous with microporous structural characteristics only, these new resins have heterogeneous structures. They consist of agglomerates of very small gelular microspheres. Each microsphere has a microporous matrix structure identical to that of

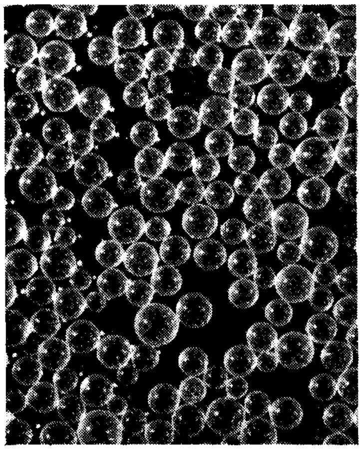

Figure 2. Gelular ion exchange resin

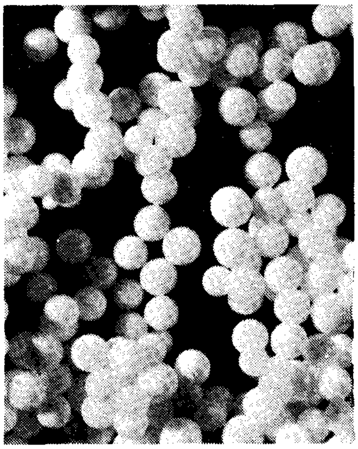

Figure 2-A. Macroreticular ion exchange resin

common gelular resins, but is much smaller than typical gelular beads. The conditions of formation are such that the very small gelular microspheres fuse into a much larger macrosphere closer in size to the usual gel bead (Figures 3, 4). In the process of microspherical fusion, pores are formed in the bead with dimensions significantly larger than the microporous dimensions of the microspherical gel phase. Rohm and Haas resins possessing macroporous character are referred to as macroreticular. The macropores are part of the rigid structure of the opaque bead resulting, and exist whether the gelular microspheres are swollen by solvent or not. Thus, whereas gelular resins have a continuous microporous matrix throughout, macroreticular resins have areas of microporous gel matrix interspersed with macropores. Reactants may move easily into the interior of the bead through these large macropores.

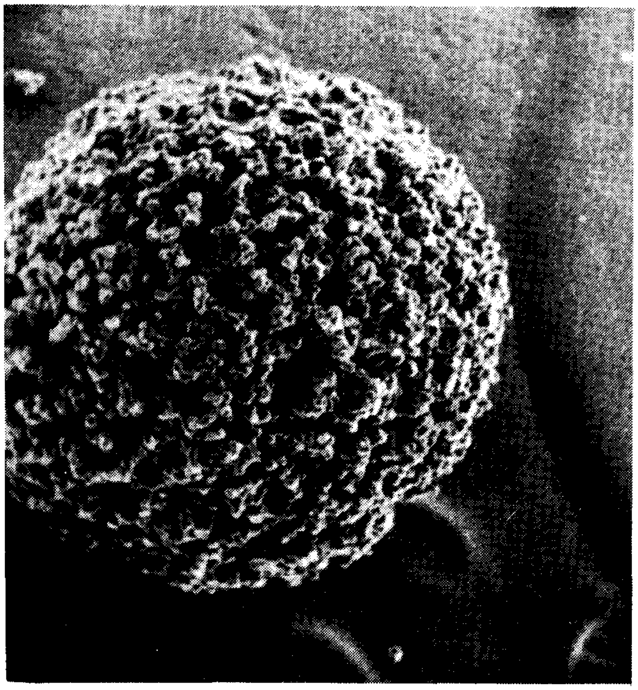

Figure 3. SEM of single macroreticular resin bead

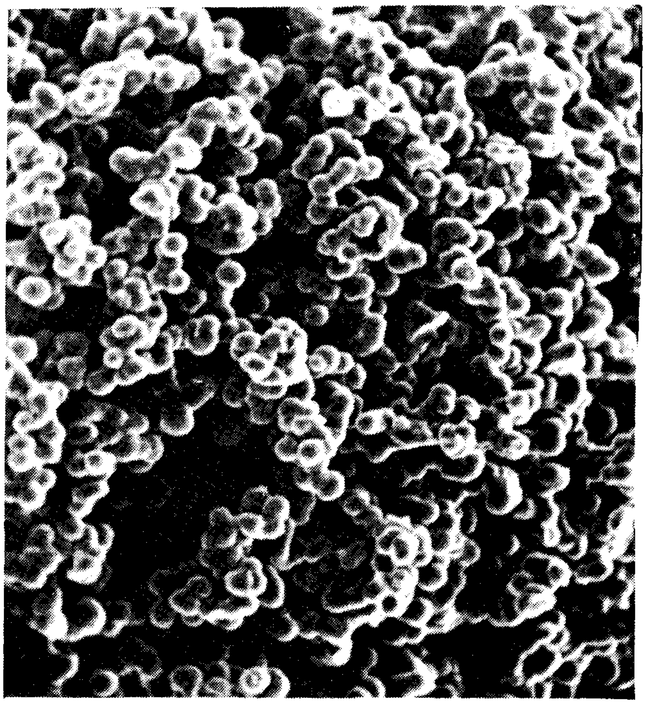

Figure 4. SEM closeup of bead in figure 3, showing fused microspherical structure

The macropore size of macroreticular resins can be controlled within limits during manufacture. Typical pore sizes for a family of sulfonic acid cation exchangers is shown in Table I.

It can be seen that as the pore size decreases, internal surface area increases. Because macroreticular resins are characterized by high internal surface area, and because catalytic sites are located on these interior surfaces, reactants migrating into these pores come in contact with many more surface catalytic sites in a macroreticular resin with an unswollen gelular phase than is possible on the exterior spherical surface of an unswollen gelular bead. The significant catalytic consequence is that, whereas gelular resins can only function effectively as catalysts in a swelling medium, macroreticular resins are effective

TABLE 1

COMPARATIVE PROPERTIES OF MACRORETICULAR STRONG ACID CATALYSTS[a]

Resin	Weight Cap. Dry Resin (meq. g.$^{-1}$)	Calculated Weight Capacity on Internal Surface (meq. g.$^{-1}$)	Internal Surface Area (m.^{2}g. $^{-1}$)	Porosity Vol. (%)	Average Pore Diameter (Å)
AMBERLYST 15	4.40	0.193	55	36	265
AMBERLYST XN-1005	3.50	0.716	120	40	175
AMBERLYST XN-1010	3.60	1.90	540	50	51

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catalysts in both swelling and nonswelling solvents, thereby greatly expanding the possibilities of resin catalysis (9, 26, 32, 36).

This advantage is illustrated in the study of the resin catalyzed dehydration of t-butanol performed by Gates (12, 13, 17). Samples of dry AMBERLYST 15 and dry gel sulfonic acid resin (2, 4, 8, 12% DVB) were mixed with t-butanol and heated. All the gel resins required an induction period before appreciable conversion to water and isobutylene was observed. During this induction period, small amounts of dehydration occurred, the water migrating into the exterior of the dry beads and swelling the collapsed matrix. The expanded matrix permitted easier access to the t-butanol, giving more dehydration, generating more water, causing further swelling, etc. When the matrix was significantly expanded, a rate increase was observed. By contrast, AMBERLYST 15 required no induction period. The t-butanol passed into the body of the beads through the macropores contacting a large number of surface sulfonic acid sites, permitting immediate dehydration. This is illustrated in Figure 5. This one experiment demonstrates both the capability of macroreticular resins for non-aqueous catalysis and the appreciable catalytic activity of macroreticular resins even in the absence of microporous swelling.

The variations in average pore diameter listed in Table 1 influence the selectivity of the bead since the parameter of pore size controls molecular entry into the interior of the bead through the rigid non-gel macropores. The macropores of these resins are, however, very large compared to most organic species of interest and movement within them would be relatively unobstructed for almost all non-polymeric molecules. The critical molecular diameters of common organic molecules are quite small by comparison to the size of the pores in even AMBERLYST XN-1010. (The critical molecular diameter is the smallest circle through which the undeformed molecule can pass). It can be seen from the data listed in Table 2 that the critical diameters of common organic species are well below the 51Å average pore diameter of AMBERLYST XN-1010 (21).

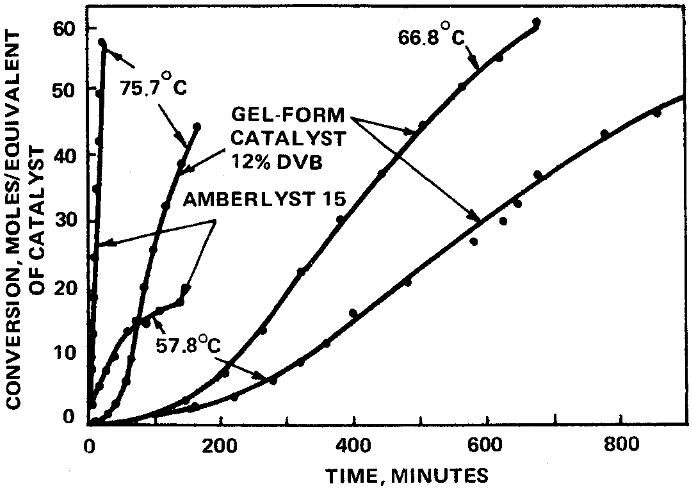

Figure 5. Comparative catalytic dehydration of t-butanol, gelular versus macroreticular resin (17)

Gelular resins exhibit only one kind of exclusion because of their homogeneously microporous character: molecules too large to fit between the solvent-swollen gelular matrix will not contact sufficient catalyst to experience appreciable catalytic activation. When swollen, macroreticular resins can also exclude large molecular species from their gelular phase. In addition, if the macroreticular gelular phase is dry, these resins still exhibit a certain degree of selectivity because their macropores will also function to exclude very large molecules while permitting smaller ones entry into the interior of the bead where appreciable surface catalytic contact occurs even when the gelular phase is unswollen. This extends the selectivity phenomenon into a significantly higher range of molecular weights.

Macroreticular resins have other advantages over gelular resins. They show excellent resistance to various types of attrition. Conventional gelular ion exchange resins shatter when some organic solvents replace the water in moist beads. Macroreticular resins undergo solvent exchange without difficulty and are inert to strong acids, concentrated alkalies, aliphatic and aromatic hydrocrabons, alcohols, ethers and most common solvents. Like all organic species, they are sensitive to high concentrations of chemical oxidants. However, macroreticular resins are far less sensitive than gelular ion exchange resins to low concentrations of oxidants. Macroreticular resins will withstand prolonged use at temperatures up to 150°C, but gradual loss in capacity may result at higher temperatures (22).

TABLE 2

CRITICAL MOLECULAR DIAMETERS OF COMMON MOLECULES

Molecule	Estimated Critical Diameter Å
Water	2.8
Isobutene	5.4
n-Heptane	4.9
Methylcyclohexane	6.6
t-Butyl Alcohol	6.4

III. ADVANTAGES AND DISADVANTAGES OF RESIN CATALYSIS

The advantage cited most frequently for the use of heterogeneous catalysts is their ease of separation from products. Their particulate nature permits mechanical separation by processes such as filtration and decantation, eliminating the necessity for product isolation by distillation or extraction procedures. Although homogeneous catalysts cannot offer this obviously important processing advantage, they do offer the benefits derived from molecular dispersion, which permits a very high degree of reactant/catalyst interaction, and they frequently exhibit increased specificity over that observed n true heterogenous catalysis.

Ion exchangers are, in effect, particulate acids and bases and when used as catalysts offer the chemical benefits of homogeneous catalysis combined with the physical and mechanical benefits of heterogeneous catalysts.

The advantages of interest in large-scale chemical processing follow:

1. The resins may be easily handled and stored.
2. Resins permit operation in either continuous or batch processes. This not only allows flexibility in process design, but also permits control of residence time in continuous operations. Neither of these features are present in homogeneous catalysis.
3. Resin catalysis simplifies the design and operation of processes by eliminating steps and equipment associated with catalyst removal, thus lowering capital and processing costs.
4. Waste disposal problems are eliminated because no waste acid or base need be discarded. Spent resins may be used as landfill.
5. Product purity and yield are improved by eliminating washing to remove catalysts. Non-aqueous systems may be kept dry throughout processing.
6. Catalyst cost per unit product can be lower than with homogeneous acid or base. Resins may be considered part of the capital investment, with cost spread over resin life, which can extend to many hundreds of cycles in well-designed processes.
7. Resins can be cleaned if contaminated. They can also be regenerated if deactivated by trace ions in the reactant. Organic foulants may be removed by washing with appropriate solvents.
8. Resin densities are close to common organic solvents and water. This permits easy dispersion throughout a large-scale batch operation with very gentle agitation. This is fortunate since the severe mechanical stresses which can lead to bead breakage are avoided.
9. Macroreticular resins permit catalysis in non-aqueous, non-polar, nonswelling solvents and reactants. Gelular matrix expansion is not a prerequisite to effect catalysis by MR resins.
10. Hydrophobic systems may be acid catalyzed by water-free macroreticular resins. These resins are much easier to dry than para-toluenesulfonic acid. Either vacuum drying or azeotropic distillation may be employed.
11. Although the acid resins contain the equivalent of strong mineral acid, they may safely be handled without danger to personnel.
12. Corrosion is eliminated or reduced significantly. Resins contain acid at much higher concentrations than can practically be employed in mild steel equipment, but the number of acid groups at the bead surface where contact with equipment occurs is a very small percentage of the acid groups present. Agitation minimizes resin/reactor contact and further reduces the possibility of corrosion.

For the chemist, the resins offer similar advantages, although the emphasis is different:

1. The acids are very strong acids. They are equivalent to concentrated mineral acids, but not as strong as the zeolite cracking catalysts. They can be used to alkylate aromatics, but not olefins.
2. The environment within the bead is equivalent to at least 1.4-2.5 N homogeneous acid. Gates and Kapura indicate acid concentrations up to 5 M of accessible acid groups in the solid phase (22).
3. Anhydrous resin can be employed in non-aqueous systems, permitting reactions not possible with aqueous acid or base. Product is isolated dry.
4. Resins are less oxidative and corrosive than corresponding homogeneous acids since almost all acid sites are within the body of the beads and comparatively less available to the product.
5. Resins offer the possibility of greater control over the course of reactions because of variable and predictable selectivity effects traceable to the matrix.
6. Application of these selectivity effects permits achievement of resin-catalyzed reactions not otherwise possible in homogeneous acid/base catalysis.
7. Macroreticular resins permit catalysis in non-polar, non-swelling solvents. No matrix swelling need occur to achieve accessibility to catalytic groups, since macroporous structure is solvent independent. Solvent choice is expanded.
8. Resins permit achievement of greater product purity by reducing or eliminating side reactions and post reactions of reactants and acids, giving higher yields. Almost all catalytic sites are buried in the beads and difficult for product to contact after diffusion from the body of the bead into the bulk solvent.
9. Resins permit achievement of greater product purity by eliminating purification procedures necessary to remove or neutralize homogeneous catalysts during product isolation steps. This also emliminates the neces-

sity for drying product subsequent to aqueous extraction procedures.

10. Resins permit achievement of reactions impractically slow by homogeneous catalysts by concentrating reactants within the beads. This advantage can sometimes be used to achieve high yields from reactants with slow reaction rates in the presence of reactants with high rates.

The major disadvantage of ion exchange resins as catalysts is the relatively low maximum temperatures of operation. Gelular cation exchange resins in the acid form should be kept below 125°C to maintain long life. The resins can tolerate temperatures up to 150°C for relatively short periods, but acid catalyzed aromatic desulfonation occurs beyond 175°C. The desulfonation can be catalyzed either by matrix-bound $-SO_3H$ or by H_2SO_4 produced by hydrolysis of these groups. Macroreticular resins can tolerate slightly higher use temperatures than gelular resins: operation at 150°C for prolonged periods is possible (22).

Anion exchange resins suffer from an even more severe limitation. Temperatures below 60° must be employed to achieve long life. Brief operation in excess of 90° is possible if shorter life can be economically tolerated. Acceptable operating conditions will most likely have to be determined empirically for each case of resin catalysis.

The apparent high initial cost of resins is deceivin In a well-designed process, the resins will be employed repeatedly, so that their cost must be considered in terms not of initial cost, but rather in terms of cost per unit product. Resins should be considered part of the capital investment. Homogeneous acid or base is comparatively cheap, but their comparative cost should be considered on a cumulative basis over the life of the resin catalyst. In addition, the cost saving associated with the reduction in equipment, simplification in processing, and elimination of waste treatment costs must also be credited to resin catalysis.

Finally, because of the favorable physical phenomena introduced by the matrix, resins could very possibly catalyze reactions in which homogeneous acid/base catalysis is ineffective. In such a case, the resin cost is justified solely on the basis of unique contribution regardless of useful life.

IV. THE MECHANICS OF RESIN CATALYSIS

In homogeneous acid/base catalysis, the acid or base is dissolved in the reaction medium and present in uniform concentration throughout the system. This is not the case with resin catalysis. No free acid or base is present. All catalytic groups are anchored to the matrix, and in the solvent-resin system are located at the surface of and within the body of the resin bead only. The bulk solvent is completely free of catalyst and consequently catalytically inert. Section III summarized the chemical and processing advantages which derive from this separation of catalyst and solvent.

Figure 6 illustrates the steps involved in gelular resin catalysis (20). Reactant present in the inert bulk solvent approaches the resin particle. Before reactant can contact the bead, it must diffuse through a convection-free layer of solvent adhering tightly to the bead, the so-called Nernst layer. Having crossed this barrier, reactant contacts the outermost chains of the polystyrene divinylbenzene matrix. If the reactant molecules do not encounter catalytic groups on the bead surface, and are small enough to fit between the polystyrene chains of the solvent-expanded matrix, they diffuse into the matrix via the solvent contained in the micropores. Reactant/catalyst interaction occurs by a chemical mechanism analogous to that in homogeneous catalysis; product results, and this in turn must diffuse back through the matrix to the surface of the bead, out through the Nernst layer, and into the inert bulk solvent, where no subsequent catalytic activity is possible. Gelular catalysis thus involves two types of diffusion: Nernst (film) diffusion which is external to the bead and therefore independent of bead composition and properties, and inner, or matrix (particle) diffusion which is influenced by those factors which affect matrix microporous dimensions on swelling.

One of these factors is the crosslink density of the gelular matrix. Two forces tend to expand the matrix: (1) the osmotic forces generated between polar solvent and the ionic exchange sites on the otherwise hydrophobic polymeric polystyrene backbone* and (2) the electrostatic repulsion between these same ionic sites (20). In the absence of crosslinks, these forces would be sufficient to eventually expand the matrix to the point where solution occurs. The crosslinks prevent chain separation. The resulting matrix is elastic and insoluble. Solvents with appropriate properties are incorporated into the matrix, which expands by osmotic and electrostatic forces until these forces are balanced by the resistance to expansion arising from the elasticity of the matrix. With any given solvent, there is an inverse relationship between the capacity of the matrix to absorb solvent and swell and the number of crosslinks per unit volume. Matrices with low crosslink densities swell significantly, giving large microporous dimensions, permitting easy entrance of reactant and rapid diffusion through the matrix. Higher crosslink densities allow less matrix expansion. Microporous dimensions are reduced, entry of the reactant into the matrix becomes more difficult and diffusion within the matrix is restricted (4, 5).

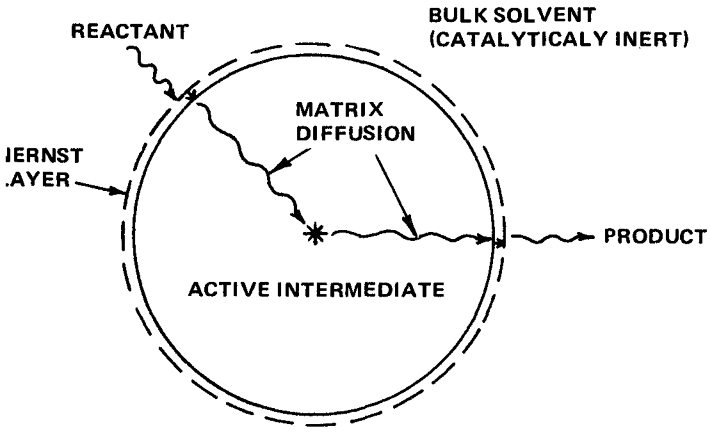

Figure 6. Schematic representing mechanism of gelular catalysis

Another means for modification of matrix dimensions depends on the variation in swelling with dielectric constant. At any given crosslink density, swelling increases with increasing dielectric constant (20). Thus, by manipulation of crosslink density and/or solvent, it should be possible to achieve microporous dimensions which permit a very high degree of reactant matrix diffusivity, while imposing a certain degree of catalytic selectivity in multicomponent mixtures.

High matrix diffusivity is a very desirable and necessary goal to efficient catalyst use. This is because of the consequences arising out of the interaction between the diffusion rates and the rate of the chemical reactions itself. At any given temperature, the rate of the chemical reaction is due almost entirely to the chemical parameters associated with reactant/catalyst interaction in the solvent-swollen micropores and is independent of matrix structure. If the rate of chemical reaction is faster than the diffusion rates, reactant cannot be supplied to the catalytic sites throughout the bead fast enough to establish equilibrium concentration. As a consequence, reaction occurs in the outer shell of the bead before the reactant molecules have time to diffuse to its core. Core catalytic sites do not

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*The unsubstituted vinyl aromatic polymeric matrix is hydrophobic and will not swell when placed in water. It is interaction between the ionic groups such as $-SO_3H$ and NR_3OH in the ion exchange resins and water which is responsible for the swelling behavior of ion exchange resins.

come into contact with reactant, and so a significant percentage of the available catalyst goes unused. This can be avoided by increasing the rate of matrix diffusion so that it is greater than the rate of chemical reaction. Reactant will then diffuse through the matrix at a rate adequate to maintain equilibrium reactant concentration throughout the bead, and all catalytic sites can contribute. The relation between crosslink density and matrix diffusion has already been discussed. Internal reaction control would most likely be achieved by employing a resin with low crosslink density. As a rule of thumb, with increasing size and/or branching of the reactant molecule, it is advisable to use the lowest crosslink density consistent with the physical demands to be made on the resin.

Reaction temperature can also influence the choice of crosslink density. The rates of diffusion processes increase less with increasing temperature than do the rates of chemical processes. Thus, as reaction temperature increases, the relative rate of the chemical reaction increases more than the diffusion rates, moving the system farther away from the conditions necessary for internal reaction control. Consequently, regardless of the size of the reactant molecule, as reaction temperature increases, the probability for internal reaction control varies inversely with crosslink density, and low crosslink density is advisable.

Another technique for increasing the rate of matrix diffusion relative to the rate of reaction involves the use of beads of very small size. The rates of the chemical reaction and matrix diffusion are independent of the size and shape of the resin particle. As spherical size decreases, the ratio of surface area to volume increases. This means that the number of surface catalytic groups relative to the number within the bead volume increases. Increase in the relative number of surface catalytic sites makes loss of the use of the sites within the bead less critical to efficient catalysis, diminishing the importance of achieving internal reaction control.

Reducing bead size can also lead to more effective catalyst use because at any given matrix diffusion rate, the finite time necessary to achieve diffusion to the core of the bead is proportional to bead size. Since a smaller bead requires less time to achieve core diffusion, the probability that core diffusion will occur before reaction occurs is increased, and internal reaction control is favored.

Although the desirability of internal reaction control dictates the use of low crosslink density and small bead size, mechanical stability and handling considerations require high crosslink density and large bead size. Gelular resins cannot satisfy these mutually exclusive requirements, but macroreticular resins offer an acceptable compromise. The fused microspherical makeup of the macroreticular beads offer small size in each microsphere, but large size in the agglomerate. In addition, macroreticular resins are characteristically more highly crosslinked than gelular resins, giving increased resistance to mechanical attrition. Gelular resins crosslinked at typical macroreticular levels would exhibit very high resistance to swelling. Reduced diffusivity and unacceptably low catalytic and/or exchange kinetics result. The macroporous character and resulting high surface area of macroreticular resins gives matrix diffusion diminished importance, and acceptable catalytic and/or exchange kinetics are possible at crosslinker levels in excess of 50 percent DVB because of the large number of surface catalytic sites available to the reactant without the necessity for matrix diffusion (see Table 1).

V. SELECTIVITY AND CATALYTIC EFFICIENCY OF RESIN CATALYSTS

Resin catalysis can offer a degree of selectivity unattainable in homogeneous acid or base catalysis. The relationship between crosslink density and microporous dimensions may be put to use as a means for selective catalysis of small molecules in the presence of large molecules. A crosslink density may be chosen to inhibit matrix expansion sufficiently so that large molecules are excluded from the interior of the bead by sieve action while small molecules may enter the matrix. Since large molecules cannot come into contact with sufficient catalyst to effect catalytic conversion, but small molecules enter the matrix and interact with catalyst, such a system is specific for the small molecules in the presence of the large. An example would be the selective acid hydrolysis of a monomeric ester in the presence of a polymeric ester. Homogeneous acid catalysis would achieve nonselective hydrolysis of all species present. Resin-catalyzed hydrolysis would leave polymeric ester untouched, while all monomer ester would be hydrolyzed. As the difference in size of the competing molecules decreases, specificity arising from sieve action also diminishes. Even when no size-related specificity is possible, however, it is sometimes possible to achieve specificity if the competing molecules have differing structures or functionality. More will be said of this in the discussion of matrix enhancement later in this bulletin.

To some degree, selectivity will influence catalytic efficiency. The efficiency of a resin as a catalyst is expressed by its q value (6) where

$$q = K_{het}/K_{hom}$$

q is the rate of the resin-catalyzed reaction compared to the rate achieved by homogeneous acid or base used at the same concentration as present in the resin. The value of q varies from less than one to greater than one. Values of q less than one are easily understood: the necessity for matrix diffusion in resin catalysis and the fixed nature of the catalyst gives the reactants reduced mobility compared to homogeneous catalysis. This may reduce the amount of catalyst/reactant interaction and thereby the product yield compared to homogeneous catalysis. However, in spite of the tortuous path reactant must traverse in all resin-catalyzed systems, some resin-catalyzed processes are characterized by q values greater than one. Such matrix enhancement is less easily understood, but nonetheless, a study of these reactions reveals a prevailing general principle which will be discussed in the section on matrix enhancement.

The efficiency of ion exchangers depends upon three factors:

1. Those properties of the catalyst and reactant which determine the activation energy of the reaction. Hammett has shown that entropy of the reactant and steric factors introduced by the matrix contribute to resin catalyst efficiency. In investigating resin-catalyzed hydrolysis of a series of esters, he was able to demonstrate an inverse correlation between ester entropy and resin efficiency (16). Similar results were observed by Affrossman and Murray (2).

2. The distribution constant of reactants between the solvent and the resin matrix. Helfferich (19) has pointed out the importance of favorable reactant distribution as a contributor to successful resin catalysis. Since high catalyst concentrations exist only within the beads, it is evident that a primary prerequisite to efficient catalysis is distribution of reactant in favor of resin phase. Otherwise, the reactant would be separated by the protecting matrix from the necessary catalytic functional groups, and little reaction would result.

3. The nature of the solvent. It is the solvent which causes the matrix to swell, which acts as the transport medium for reactant, and which to a large extent controls distribution of reactant between the solvent and the resin phase. Solvent choice is thus of fundamental importance in establishing the value of q. In some cases of aqueous catalysis, it is necessary to add an organic solvent to solvolyze a water-insoluble reactant. In such cases solvent distribution may also occur which can alter the reactant distribution and profoundly alter the value of q. The work of Davies and Thomas (11) and Haskell and Hammett (16), to be discussed in the section on Reaction Types, illustrates this, and points out the importance of solvent on catalytic efficiency. Indeed, it is no exaggeration to say the choice of solvent is one of the most important variables available in resin catalysis, and considerable attention should be given to solvent selection to insure the most favorable distribution of reactant. Of course, the solvent chosen must be an effective solvent for both reactant and product, since formation of an insoluble product inside the matrix would effectively terminate catalytic activity.

VI: MATRIX ENHANCEMENT

In cases of resin catalysis in which the efficiency factor q is greater than 1, the phenomenon of matrix enhancement is operative. Matrix enhancement results when the matrix acts to increase the number of reactant/catalyst contacts over those obtained in homogeneous catalysis at equivalent reactant/catalyst concentrations.

The contributions made by this phenomenon are unique to polymer-bound catalysts and arise from a variety of causes. Once understood and employed, matrix enhancement permits a degree of control and a level of efficiency impossible in homogeneous acid/base catalysis.

The chemistry of matrix-bound sulfonic acid or tetraalkylammonium hydroxide moieties will not be appreciably different from that of their homogeneous counterparts at acid or base concentrations identical to that existing within the bead. Attachment to the matrix does not add to or detract from the catalytic powers of the acid or base; reactions susceptible to homogeneous acid or base catalysis should be just as susceptible to catalysis by resin-bound acid or base. Nonetheless, the action of the bound catalysts is different because of the physical effects introduced by the matrix, whether these be favorable or unfavorable. Unless the catalytic sites contribute to the overall crosslink density of the matrix by themselves acting as crosslinkers, the matrix effects arise essentially independent of the nature and identity of the catalytic moieties, and are due mainly to the diffusion phenomena characteristic of resin-bound catalysis, to the selectivity introduced by the matrix, and to solvent/resin reactant distribution (10,14). In all cases of matrix enhancement, conditions are such that either selectivity has been enhanced by some structural characteristic of the matrix, or the solvent used increases the tendency of reactant to move into the body of the bead. The effect of both is to increase the reactant/catalyst ratio over that achieved in homogeneous catalysis under similar conditions, which in turn increases the degree of conversion of reactant to product. This possibility for controlled influence of reactant/catalyst ratio is an advantage unique to resin-bound catalysis. The following examples illustrate this capability.

The reaction of furfural with aldehydes is base catalyzed. Two competing reactions occur: aldehyde with furfural, and aldehyde with aldehyde. In aqueous base, the latter proceeds at a faster rate than the former, so that almost no reaction of aldehyde with furfural is observed. Self-crotinization of the aldehyde is preferred. When a strongly basic resin is employed as the catalyst, the furfural concentrates in the microporous structure of the bead. Since the bulk solution in a resin-catalyzed system is inert, the aldehyde cannot undergo significant catalysis until it migrates into the body of the bead. When it does, it meets a high concentration of furfural, and even though the kinetics may be no more favorable, the high concentration of furfural favors reaction between aldehyde and furfural rather than between aldehyde and aldehyde. Here, the matrix enhances the rate of production of the desired product by acting as a medium for concentrating one of the reactants in preference to the other. Such an effect is impossible in homogeneous catalysis. This type of matrix enhancement can only occur when the reactant having the slower rate concentrates in the bead. If the reactant with the faster rate is preferentially concentrated in the beads, the undesired reaction proceeds. This is an example of a reaction in which gelular resins are preferred catalysts. Self-crotonization could well occur in the macropores of a macroreticular resin since the aldehyde/furfural concentrations in the macropores are close to those in the bulk solvent and a high concentration of surface catalytic sites are available to catalyze self-crotonization.

Matrix enhancement can also occur if the reactant is only sparingly soluble in water. The matrix can exert a solvating effect on the organic reactant, achieving a higher relative concentration of reactant to hydrated protons than possible otherwise. This is the effect observed by Davies and Thomas in the hydrolyses of esters of various molecular weights where the relative rate of resin catalysis to homogeneous catalysis increased with the molecular weight of the ester (11). This enhancement occurs when a reactant with a hydrophobic structure is resin-catalyzed in pure water. The solvent inside and outside the bead is pure water. The organic reactant shows preferential solubility in the organic matrix, raising the relative concentration of reactant to catalyst above that achieved in homogeneous catalysis at identical reactant/catalyst concentrations. The more hydrophobic the structure, the more matrix concentration is favored, and the greater the enhancement.

In the next two examples, matrix enhancement occurs because of a modification made to the catalytic group. The term matrix enhancement still applies, however, because the success of the modification results from the modified group being anchored to the matrix. The same combination of components mixed in a homogeneous system produces no enhancement.

Because resin catalysts are ion exchange resins, they may be modified by exchange with appropriate ionic species. In the case of ester hydrolysis, Riesz and Hammett (33) have shown that partial substitution of H^+ ions by quaternary ammonium cations results in an increased rate constant for the heterogeneous reaction. This was attributed to the increase in the distribution constant resulting from the introduction into the resin matrix of mobile ions similar to the reactant, hence, the increase in q. The effect was fairly specific. For instance, they found that replacement of 70 percent of the hydrogen ions by benzyltrimethylammonium ions favored hydrolysis of methyl phenylacetate, whereas replacement of 70% of the hydrogen ions by cetyltrimethylammonium ions favors hydrolysis of ethyl-n-hexanoate. Thus, if the appropriate organic ions are available, the chemist may modify a matrix at will to increase the distribution constant of reactant in favor of the matrix.

The protons in acid resins may also be exchanged with metal ions. Affrossman and Murray (1) report that substitution of hydrogen by silver ions increases the efficiency of a sulfonic acid resin for hydrolysis of unsaturated esters. Substitution of hydrogen ions with potassium ions reduces the efficiency of the resin for hydrolysis of both propyl acetate and allyl acetate (Figure 7). This is because the potassium in no way favors distribution of reactant in the resin, but merely serves to dilute the catalyst level. Displacement of hydrogen ions by silver ions likewise reduces catalytic efficiency for propyl acetate hydrolysis, but because of the interaction between the silver ions and the double bond in allyl acetate, the distribution of allyl acetate in the resin is highly favored and hydrolysis proceeds with great facility, even when as much as 90% of the protons are displaced by silver ions (Figure 8). This not only demonstrates another technique for matrix enhancement, it also suggests the possibility for selective catalysis of double bonded species in the presence of saturated reactants.

A general principle emerges from the examples given: any means by which the relative concentration of reactant to catalyst can be increased over that achieved in homogeneous catalysis should result in matrix enhancement and a catalytic efficiency greater than 1.

Since the distribution of reactant between resin and solvent rests largely on the properties and nature of the solvent, it becomes evident that solvent choice is one of the most import considerations in matrix-bound catalysis.

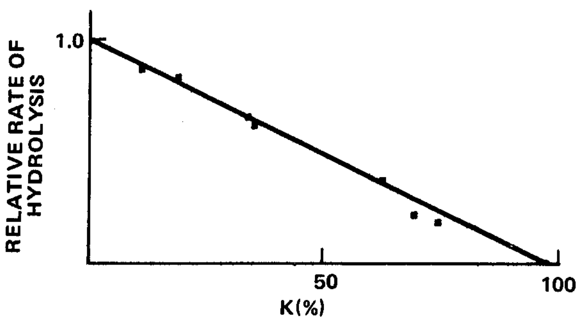
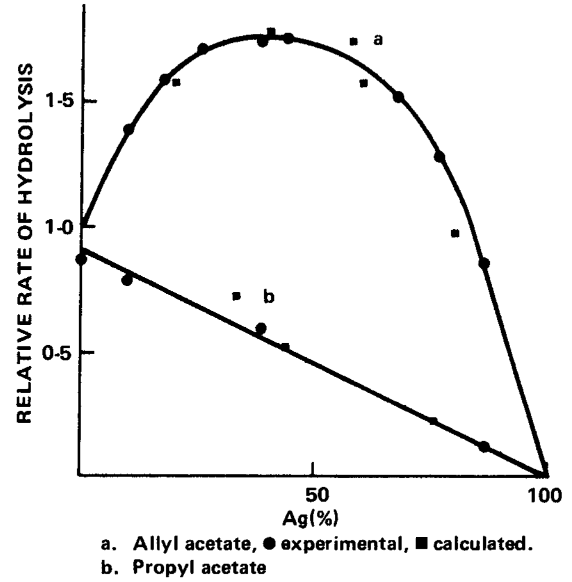


Figure 7. Hydrolysis of allyl acetate by a K resin at 27.5°



a. Allyl acetate, ● experimental, ■ calculated.
b. Propyl acetate

Figure 8. Hydrolysis of allyl and propyl esters by Ag resins at 27.5°

VII. FOUR TYPES OF SULFONIC ACID RESIN CATALYSIS

The major portion of the literature describing acid resin catalysis involves dissociated sulfonic acid in hydrated resins. Recently, Gates published a series of fundamentally important papers describing catalysis by anhydrous sulfonic acid. These papers showed the catalytically active species and the reaction mechanism to be completely different from that observed in the presence of water (12, 35, 36). Comparison of this new literature with the early literature reveals an important relationship between the solvent system and the nature of the catalytic species.

Simply stated, the presence or absence of low levels of water establishes whether the catalytic agent will be the solvated proton or the undissociated sulfonic acid group, respectively. This understanding of the influence of small quantities of water is comparatively new and can be traced to the infrared studies of Zundel (37). The capability for anhydrous catalysis introduced by macroreticular resins makes knowledge of the catalytic consequences of low levels of water important to the effective use of these acid catalysts.

In addition to the importance of water content, those conditions which influence the distribution of reactant between bulk solvent and resin matrix are also critical to the success of resin catalysis. The influence of solvent varies depending on whether the solvent is pure water, water/organo solvent, or pure organic solvent. In the latter case, polar and non-polar solvents exert differing influences, also.

Thus there are two forces at work which affect catalytic efficiency: water content controls the nature of the catalytic species and therefore catalytic effectiveness; the solvent controls the distribution of reactant in the bead and thus the level of catalyst/reactant contact. In some cases, these forces might reinforce each other, in other cases, they may be in opposition.

This complicated picture can be brought into focus by means of the following classification, which is suggested as a means to aid understanding of the various systems described in the literature. In addition to permitting a label to be applied to the mechanism operative in acid resin catalysis, the classification emphasizes the extreme importance of solvent character and composition in resin catalysis.

Essentially all of the resin catalyzed reactions in the literature fall into one of two major types.

In Type A systems, there is present sufficient water to solvate all the protons present in the sulfonic acid resin, so that it is the solvated proton which is the active catalytic species. Type A may be broken down into two subtypes, depending on whether or not an organic solvent has been employed to solubilize a water-insoluble reactant.

The second major Type, B, arises in the absence of water and involves catalysis by the undissociated sulfonic acid group. The subtypes are determined by the reaction itself, depending on whether or not water is a product of reaction. Generation of water of reaction results in eventual transition of a Type B reaction to a Type A reaction. This is undesirable. Gates (13) has shown the undissociated sulfonic acid group to be some forty times a better catalyst than the solvated proton. Water acts as an inhibitor and reduces catalytic efficiency. Steps may be taken to maintain B character, as described below. The four types may be summarized as follows:

Type A (H+)	1. Catalysis by fully water-swollen resins in aqueous systems. 2. Catalysis in mixed water/organo solvents.
Type B $(\text{-SO}_3\text{H})$	1. Catalysis by water-free resins in non-aqueous systems where water is not a product of reaction. 2. Non-aqueous catalysis in which water is a product of reaction.

Types A1 and A2

Catalysis by fully water-swollen resins in aqueous or polar systems is most closely related to true homogeneous acid/base catalysis. In this type of acid resin catalysis, the hydrated proton is the catalytic agent. Although the resin beads are discrete particles, catalysis by gelular ion exchange resins in aqueous or polar systems is not a case of true heterogeneous catalysis, but is more accurately described as homogeneous catalysis within the pore liquid in the bead, a quasi-homogeneous catalysis. It is as if the bead were, in essence, a very small reaction kettle isolated from the bulk solvent. The pores of an ion exchanger in contact with an aqueous or polar solution contain solvent, solute and counter ions. The counter ions are mobile and solvated and therefore, in principle, not different from ions in a corresponding homogeneous solution. Consequently, it is expected that in aqueous or polar systems, the reaction mechanism in homogeneous catalysis by a dissolved electrolyte and heterogeneous catalysis by a resin is essentially the same (20). Experimental observation has shown that the order of the actual chemical reaction is the same for aqueous homogeneous acid/base catalysis and for quasi-homogeneous ion exchange catalysis, and that the activation energy is similar (7). For example, it has been reported that the catalytic activity of sulfonic acid and sulphonated polystyrene resins towards the dehydration of tetracycline is determined only by the strength of the acid contained and is independent of the concentration of water and divinylbenzene in the resin. This constitutes evidence for the contention that the catalytic activity of H^+ ions is the same in the resin and in the acid phase and is the basis for the comments made on the chemical nature of the acid or base being independent of the matrix. This applies, of course, only when there is sufficient water to hydrate all protons to permit complete dissociation. Undissociated sulfonic acid groups react differently as described below.

What differences exist between true homogeneous and quasi-homogeneous catalysis arise because in the resin, for the most part, the reactions occur within the pore liquid contained between the matrix of the gel phase, so that the physical phenomena of reactant and product diffusion are involved. Also, the nature and proximity of the matrix and fixed ion groups create an environment for reaction different from that in bulk solution which may or may not affect the reaction.

Perhaps the most important reason for observed differences between homogeneous and quasi-homogeneous reaction is due to the possibility that the reactant may demonstrate preferential solubility in the matrix because of reactant/matrix interaction (19). As a consequence, the rate of heterogeneous resin catalysis is enhanced over the rate of homogeneous catalysis. This is particularly true when the reactants are only sparingly soluble in water.

Hydrolysis and hydration are typical Type A1 reactions. Resins have been used for the hydration of hydrocarbons with double and triple bonds; specifically, tertiary pentenes, propene oxide, 2 methylpent-1-ene, acetylene, 2-dioxymethylnorbornene-5, and hydrocarbons with lactone rings (30, 31).

The water content of the resin plays a part in the course of the hydration. As the water level of the gel phase increases, the strength of the bond between water molecules and sulphonic acid groups decreases, making addition of water to the double bond easier.

In the absence of any organic solvent, resin-catalyzed Type A reactions of organic species can benefit from the organic nature of the matrix itself. This is very evident from the work of Davies and Thomas in their study of the resin-catalyzed hydrolysis of a series of esters using pure water as the solvent, a Type A1 system (11). They showed the efficiency of AMBERLITE IR-100* in the hydrolysis of a series of esters in aqueous solutions exceeded unity, increasing with increasing molecular weight of the ester undergoing hydrolysis. The resin was found more effective than hydrochloric acid by factors 1.8 for methyl acetate, 8.3 for ethyl acetate, 10 for n-butyl acetate and 20 for benzylacetate.

The importance of the solvent system on the efficiency of resin catalysis is emphasized by the experience of Haskell and Hammett, who studied the hydrolysis of methyl and ethyl acetates, ethyl n-butyrate and ethyl n-hexanoate dissolved in 70 percent acetone using AMBERLITE IR-120, a Type A2 system (16). They found HCl catalytically more efficient than the resin by factors of 2 for methyl acetate, 3 for ethyl acetate, 7.5 for ethyl butyrate and 20 for ethyl hexanoate.

The difference between Haskell and Hammett's, and Davies and Thomas' results can be attributed to the distribution of solvent between ion exchanger and liquid phase. The ion exchanger is enriched by the solvent with the higher dielectric constant, while the concentration of acetone in the liquid phase rises. Davies and Thomas showed that 10% DVB crosslinked polystrene, when equilibrated with 70 percent acetone, has liquid within the resin consisting of 72 percent water and 28 percent acetone, whereas the composition of the outer solution was 75% acetone and 25% water. The distribution of an organic substrate between these two phases would be greatly in favor of the bulk solution containing mainly organic solvent, rather than the interior of the resin which contains mainly water. This is especially true for long chain esters which are sparingly soluble in water. The ester concentration rises in the liquid phase enriched by the organic solvent, the solubility increasing with the length of the hydrophobic radical. That is, the rate of ester hydrolysis increases or decreases as the solubility of the ester in the resin versus the surrounding solvent increases or decreases.

This contrast in resin effectiveness as a function of solvent composition points out the importance of the reaction conditions in achieving success in resin catalysis. In a completely aqueous system, the resins would be judged useful and effective whereas in the 70 percent acetone solution, homogeneous acid catalysis would be preferred. Conditions influencing reactant distribution are crucial to the success of resin catalysis.

Mercier (27) describes the effect of low levels of water in the resin catalyzed synthesis of mesityl oxide. By using a water-acetone mixture containing 1-3% water, he was able to continuously desorb high boiling by-products and maintain the resin in active form five times longer than in the absence of water. By contrast, the activity of the catalyst is completely destroyed when the water concentration is increased to 10%.

These examples illustrate the importance of the correct choice of reaction conditions in any evaluation of resin catalysis, and suggests that the cause of failure in any attempt at resin catalysis is as likely to be due to the wrong set of conditions as it is to inability of the resin to accomplish catalysis. Further, the first example illustrates the importance of minimizing the quantity of any organic solvent used to solubilize a water insoluble organic reactant (7, 8).

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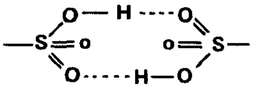
*AMBERLITE IR-100 is no longer offered by Rohm and Haas. AMBERLITE IR-120 is an acceptable substitute.

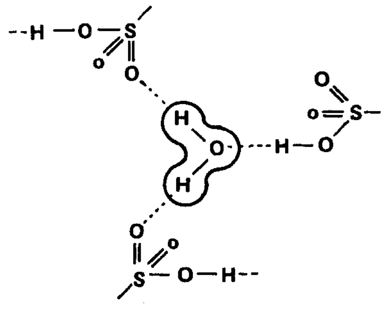
Types B1 and B2

Types B1 and B2 catalyses are completely anhydrous and include reactions of significant commercial importance. One such reaction is the alkylation of phenol (9). Octyl, nonyl and dodecyl phenol are all produced by resin catalysis using AMBERLYST 15 as the catalyst. In this reaction, the alkyl adds by direct replacement of hydrogen on the benzene nucleus. Para substituion predominates unless this position is occupied, then ortho substituion occurs. Structure plays an important part in alkylation reactions. Increasing the number of substituents on the nucleus of the compound to be alkylated, and branching of the hydrocarbon chain of the alkylating agent produce lower yields of alkylphenols.

Water has a detrimental effect on the yield of alkylphenols. Yields drop sufficiently in the alkylation of phenol to necessitate removal of the resin and replacement by dry resin. This drop in catalyst activity with addition of water is typical of Type B1 reactions which are catalyzed by the undissociated sulfonic acid group rather than the hydrated proton. Such is the case in both alkylation reactions and dehydration reactions. The cause for this deactivation was described in some fundamental infrared spectroscopic studies performed by Zundel (37). In his work, Zundel prepared extremely thin films of styrene-divinyl benzene sulfonic acid cation exchanger. By means of infrared analysis, Zundel showed that the sulfonic acid groups in completely anhydrous sulfonic acid resin are paired by formation of a doubly hydrogen-bonded structure.

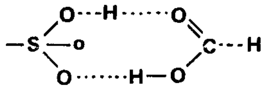


Zundel very carefully added minute quantities of water to the anhydrous film and found that at low water concentrations, the water molecule is strongly bonded to three sulfonic acid groups.

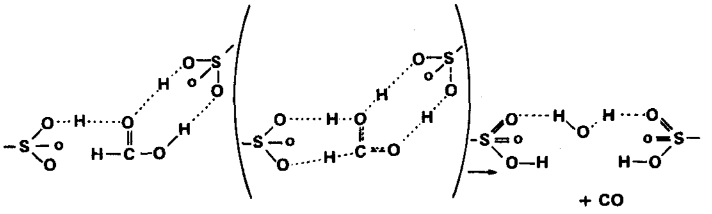


A fourth sulfonic acid group may be similarly bonded to the remaining electron pair of the water oxygen.

Gates used Zundel's technique as a tool for the elucidation of the effect of water on the reaction mechanism of anhydrous sulfonic acid resin catalysis by studying the dehydration of formic acid (12) a Type B2 reaction. Infrared spectroscopy showed that formic acid contained in a thin film of completely anhydrous sulfonic acid resin was bound to the sulfonic acid sites by hydrogen bonds.



Gates proposed the following mechanism for the resin catalyzed dehydration of formic acid.



Water in the matrix suppresses the formic acid reaction by binding to the sulfonic acid groups in competition with reactant. This converts the initially very efficient Type B2 reaction to Type A1 reaction. Reduction in catalytic activity follows because the solvated proton is not as available to a reactant as is the very labile proton attached to the undissociated sulfonic acid group. Zundel observed that only two water molecules per sulfonic acid group were sufficient to convert all the protons to their solvated state (38). Thus, this undissociated catalytic species is very sensitive to water and the resin must be kept very dry to maintain high catalytic activity.

Zundel found the residual water content on drying was a function of the severity of the drying conditions. When hydrated resin is rapidly dried at 150°C, all of the water is removed. When drying is slow, water is hydrogen bonded to $3SO_3H$ groups and cannot be removed even under severe conditions (38).

Thornton and Gates describe the infrared technique used to follow B1 and B2 reactions in their study of olefin and paraffin formation from butyl alcohols (35). This work demonstrated that alcohols could also inhibit reactions by competing with reactants as does water. The suggestion is made that the catalytic efficiency of sulfonic acid resins is due to the strong proton-donating and proton-accepting tendencies of the network of sulfonic acid groups existing within the matrix, and detailed mechanisms are described.

Type B2 reactions include any anhydrous reaction in which water is a product of reaction, such as dehydration of alcohols, or synthesis of esters from acids and alcohols. Because the active catalytic species is the undissociated sulfonic acid group, and because transition from B1 or B2 to A1 catalysis occurs with only trace quantities of water, it is necessary to take steps to consume any water generated to maintain B character.

The technique used to counteract the formation of water in ester synthesis is illustrative of the kind of solution possible; anhydrides are added with the alcohols, and olefins, olefins oxides or olefin carbonates are added with the acid. This consumes the water and increases the yield of ester (31).

Esterification is one of the most active areas for application of resin catalysis. The resins have been used for direct esterification, or transesterification. With low molecular weight acids and alcohols, the structure of the network has almost no effect on the yield of the ester or the kinetics of reaction. As the reactant molecular weights increase and consequently their value as swelling solvents diminshes, the structure of the three-dimensional network becomes increasingly important. The potential benefit of macroporous resins becomes more obvious as the accessibility of the sulfonic acid groups becomes more important, since diffusion into the matrix is inhibited and surface reaction increases in importance.

The rate of esterification by resin catalysis decreases, just as it does in homogeneous catalysis, as the chain length of the aliphatic radical on the alcohol or acid is increased. The yield of ester is also a function of the reactant structure; normal alcohols give esters in higher yields than their isomers. The yield is also sensitive to the molar ratio of alcohol to acid. Esterification in the presence of excess alcohol leads to swollen beads, which accelerates the reaction. The presence of excess carboxylic acid does not swell the resins appreciably and the reaction is slower than when the reactants are present in equimolar proportions.

Use of resin catalysis in tranesterification avoids the problem of transition from B to A catalysis which arises because of product water.

VIII APPLICATIONS OF RESIN CATALYSIS

Resins have been used as catalysts for hydration, hydrolysis, alkylation, esterification, transesterification dehydration, polymerization and condensation reactions, and as isomerization catalysts (24, 29, 30, 31). On a commercial scale, ion exchange catalysis has found practical application in a number of large-scale industrial processes. AMBERLITE IR-118 (H) is used extensively in continuous systems to effect the inversion of sucrose to invert sugar. AMBERLYST 15 is used by Rohm and Haas and other major chemical manufacturers as a non-aqueous catalyst for the alkylation of phenol (9). Neier and Woellner describe the use of a sulfonic acid cation exchanger as a catalyst for the direct hydration of olefins to form isopropyl alcohol (28). Other large applications exist but are proprietary. It suffices to say that ion exchange resins are well established as economical catalysts in a wide spectrum of industrial processes and the large number of evaluations currently being pursued should result in even wider use.

The extensive patent literature describing the use of ion exchange catalysts gives some clues to the applications of interest. Much of the literature is summarized in a bulletin published by Rohm and Haas. Requests for the bulletin entitled "Patented Applications of Resin Catalysis" should be directed to the Fluid Process Chemicals Department, Philadelphia, PA 19105.

Issues #127, 128, and 135 of AMBER-HI-LITES have detailed many uses for resin catalysts, as well as summarized the properties of Rohm and Haas resins found suitable for catalytic applications. These issues are included for your reference.

IX. LABORATORY-SCALE SYSTEMS FOR ION EXCHANGE CATALYSIS

A brief description of several types of laboratory-scale setups is presented as a guide to those considering the use of resin catalysis. The descriptions are taken from the literature and are meant to give the experimenter only enough information about the apparatus and process to indicate their potential utility in his work. The original references should be consulted for details.

Batch Operation

Heath and Gates (17) used the apparatus pictured in Figure 9 for the batch catalysis of the dehydration of t-butyl alcohol. Liquid reactant contacted suspended beads of catalyst in a flask maintained at constant temperature. In this experiment, reaction rate was conveniently monitored by measurement of isobutylene generation using a wet-test meter. In any batch operation, the experimenter is cautioned to use a stirring rate no higher than necessary to maintain the beads in suspension. Rapid stirring can result in mechanical attrition. This setup can be used for resin catalysis of a single liquid reactant, for a preformed mixture of reactants or, by addition of a dropping funnel to the apparatus, for incremental addition of one liquid reactant to another.

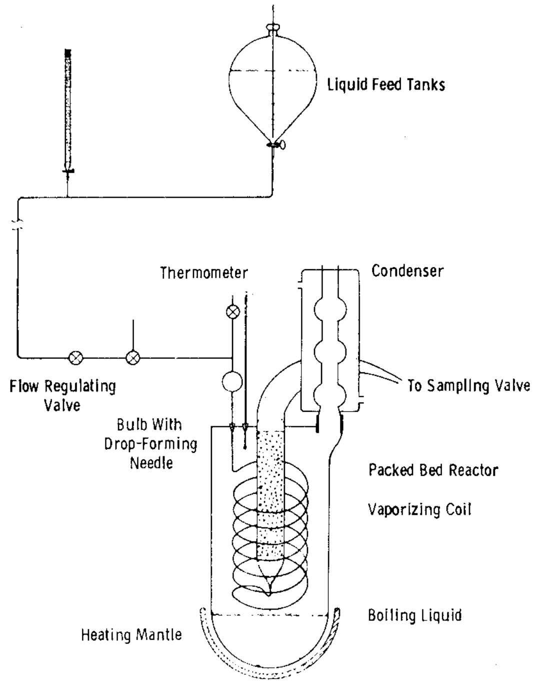


Figure 10. Reactor system employing a fixed resin bed and a reactant preheater

Continuous Systems

Three different types of continuous systems are described by Gates and Schwab, Kapura and Gates, and Tedeschi et al. The first system was employed for the continuous catalytic dehydration of formic acid (12). The reactor system pictured in Figure 10 was a glass tube 3 cm in diameter and 10 cm long. Reactant was fed through a vaporizing coil which in turn was built into a vessel in which boiling organic liquids provide constant temperature. Catalyst was mixed with glass beads and packed into the reactor. Reactant liquid flowed from two constant-head tanks through a vaporizing coil, upward through the reactor and through a heated exit tube to the vapor sampling tube of a gas chromatograph. This is a fixed bed system suitable for catalysis of a single liquid reactant which can be either a pure liquid or a mixture.

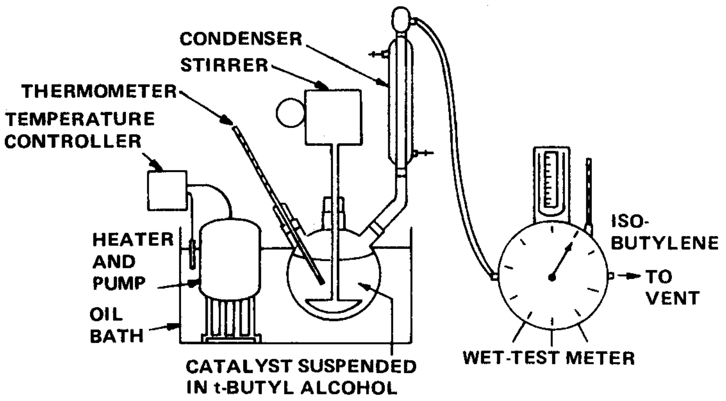


Figure 9. Batch reactor system

The second continuous system permits reaction between a liquid and a gas and employs the setup pictured in Figure 11 (22). A packed-bed flow reactor was enclosed in a furnace. In the work described, benzene and propylene were fed into the reactor at controlled rates and the product stream monitored by gas chromatography.

A more sophisticated system combining features of batch and continuous modes is pictured in Figure 12 (34). This apparatus was employed for the continuous isomerization of tertiary vinyl carbinols. Unlike the two previous systems which employed a fixed resin bed, the resin in the isomerization chamber was stirred during use. Again, the experimenter is cautioned to avoid excessive stirring rates to minimize mechanical attrition.

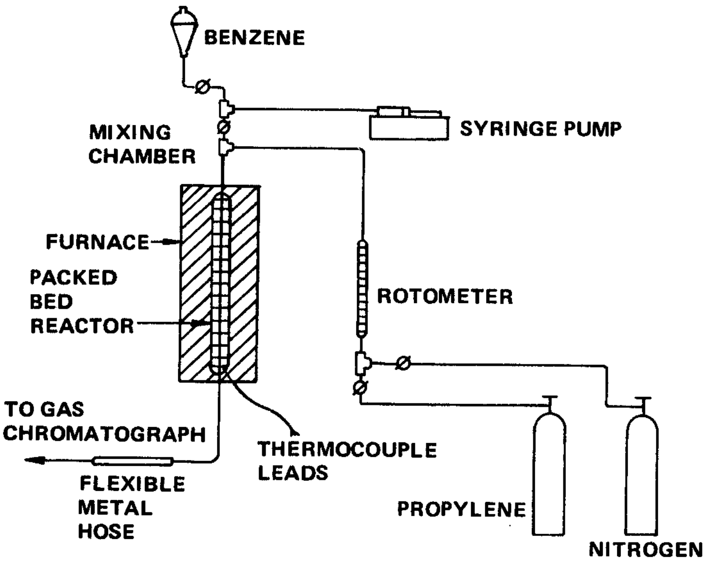


Figure 11. Schematic diagram of reactor system for gas-liquid reaction

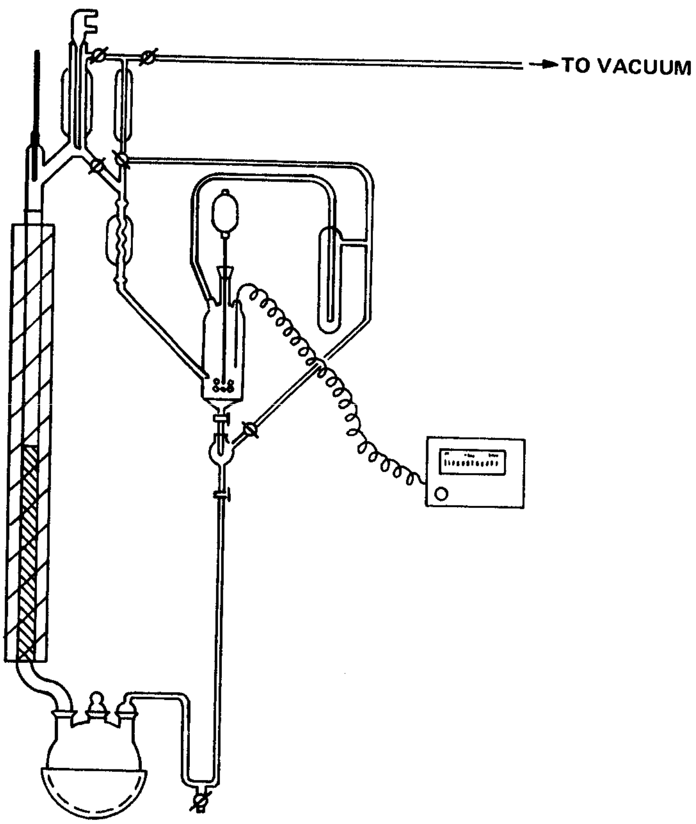
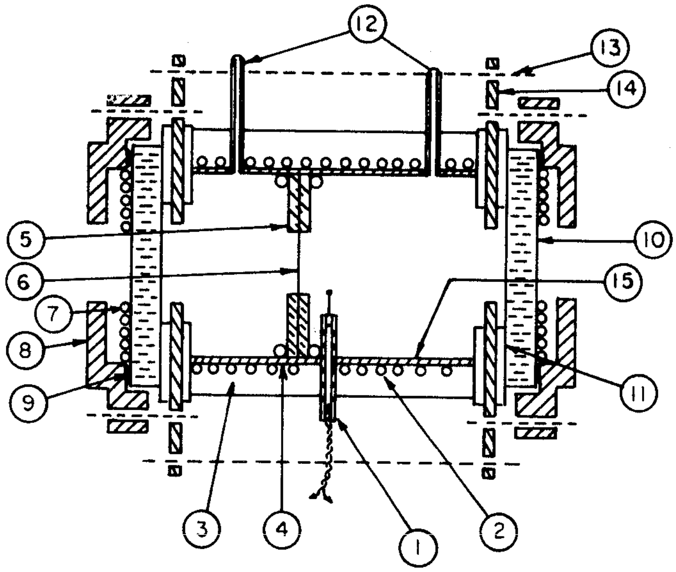


Figure 12. Continuous isomerization system employing stirred resin

Continuous Reactor with Infrared Monitoring

Thornton and Gates (35) described the apparatus pictured in Figure 13. The cell was designed to permit monitoring of the infrared spectrum of the sulfonic acid groups of a sulfonated styrene-divinyl benzene membrane while in use as the catalyst inside the cell. Rearrangement of the various elements of the cell so that the infrared beam passes through the reaction chamber parallel to the membrane rather than through it as shown in Figure 13 might permit continuous infrared monitoring of either reactant or product, depending on which side of the membrane the beam passes.

Many variations on these systems are possible. All systems, however, should be designed to take into consideration the limited thermal stability and mechanical properties of the resin beads.



(1) thermocouple in thermowell
(2) cell body heater wires
(3) insulation
(4) spring rings
(5) Teflon gauze supports
(6) catalyst membrane
(7) window heater wires
(8) brass window clamps
(9) paper washer
(10) NaCl windows
(11) silicone rubber gaskets
(12) inlet and outlet tubes
(13) securing bolts with collars
(14) stainless steel end plates
(15) stainless steel cell body. Cell length and diameter were 5 cm.

Figure 13. Details of infrared cell flow reactor construction

SAFE HANDLING INFORMATION

Caution:

Acidic and basic regenerant solutions are corrosive and should be handled in a manner that will prevent eye and skin contact. In addition the hazards of other organic solvents should be recognized and steps taken to control exposure.

Nitric acid and other strong oxidizing agents can cause explosive type reactions when mixed with ion exchange resins. Proper design of process equipment to prevent rapid buildup of pressure is necessary if use of an oxidizing agent such as nitric acid is contemplated. Before using strong oxidizing agents in contact with ion exchange resins, consult sources knowledgeable in the handling of these materials.

A Material Safety Data Sheet is available for Amberlite and Amberlyst Ion Exchange Resins. To obtain copies for specific resins contact your Rohm and Haas representative.

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CATALYSIS WITH ION EXCHANGE RESINS

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Introduction

One of the most fascinating and intriguing aspects of chemistry is the area of catalysis.

Well over a century ago, J. J. Berzelius, one of the founders of modern chemistry, observed that the course of some chemical reactions was influenced by the presence of certain substances which were unaltered in the process. The influence or "force" that these substances exhibited on the course of reactions was called catalysis (Greek: loosen) by Berzelius who reasoned that certain "forces" had to be "released" before certain reactions could proceed perceptibly.

Many of the more important industrial and biological chemical processes would normally proceed at infinitely slow rates of reaction were it not for the "magic" of catalysis. Certain substances, known as catalysts, are able to increase chemical reaction rates without being altered as a result of the reaction. These catalysts do not change the ultimate nature of the reaction. They merely alter the speed with which the chemical reaction takes place. In other words, they do not influence the thermodynamics or equilibria of chemical reactions. Their function is one of influencing the kinetics of the reactions. The term catalyst cannot be defined in terms of composition and is best defined by its behavior. The following criteria are usually considered as defining a catalyst:

1. While influencing the rates of a reaction, the catalyst remains unchanged chemically.
2. A small amount of catalyst is all that is required for it to function.
3. The catalyst does not alter the equilibrium of the reaction.

There are but few chemical processes that would be of value to industry were it not for the phenomenon of catalysis. The ability to produce and to make available at reasonable costs on a worldwide basis such critical chemicals as ammonia, nitric acid, sulfuric acid, synthetic polymers, etc. is the result of discoveries that various substances can act as catalysts for the chemical reactions upon which these products are based.

The role of catalysis does not limit itself to the world of industrial chemistry. Most of the chemical reactions upon which biological processes are based depend upon very complicated catalytic processes. In the case of the biological processes, the catalytic agents are known as enzymes. The ability of living organisms to digest food, to derive energy from food, to synthesize life-required compounds, etc., etc. are all dependent upon reactions catalyzed by enzymes.

There are many, many substances that can act as catalysts for chemical reactions. These range from simple inorganic compounds which can be synthesized in the laboratory to the extremely complicated organic enzymes which can only be found in living systems. Although there are but few areas of chemistry that have been studied as exhaustively as the phenomenon of catalysis, our fundamental understanding of the mechanism by which catalysts function is still quite vague. For example, the synthesis of ammonia from molecular hydrogen and nitrogen, $N_2+3H_2 \rightarrow 2NH_3$, which depends upon the catalytic properties of a particular crystalline form of iron oxide containing minor quantities of aluminum and potassium oxides, has been studied by the most eminent of chemists for more than half a century. However, the fundamental function of the catalyst still eludes us. Current theory suggests that the catalyst provides a lower energy path for the reaction than is required by the un-catalyzed reaction.

In spite of our lack of understanding the fundamental mechanism of catalysis, much information has been amassed that permits one to relate the chemical and physical properties of certain substances to their ability to catalyze various reactions. For example, some reactions are catalyzed by acidic substances whereas some reactions require basic substances as catalysts. There are other reactions that are catalyzed by the surfaces of metals in their elemental form. Catalytic properties, however, are not limited to acids, bases, and metals. Various salts, organo-metallic complexes, and a host of such solids as the carbons, aluminas, etc., also have catalytic properties for various reactions. The choice of catalysts for various reactions is based primarily upon past experience and oft-times is based upon a trial and error approach. On a number of occasions, frustration over many abortive attempts to find a suitable catalyst for a reaction has been overcome by a "last effort" attempt to try whatever chemical that was handy on the chemist's shelf.

The catalysis of various reactions may be conducted homogeneously or heterogeneously. In the case of the former, the catalyst is dissolved in the reaction mixture. In the latter case, the function of the catalyst depends upon contact of the reactants at the surface of the catalyst. Some reactions can be catalyzed by either type of catalyst system.

Catalysis by means of ion exchangers has been the subject of study for more than half a century. It is of interest to note that the effective acidity of the cation exchange complex of the soil was measured in terms of its catalytic effect on the hydrolysis or inversion of sucrose solutions. In other words, the overall effective acidity of soil suspensions was measured years ago by their catalytic activity. Although pH measurements might now be considered a more direct measure of acidity, a half century ago, polarimetry (a means for measuring sucrose inversion) was considerably far more advanced than the measurement of pH. Whereas the catalytic activity of ion exchange systems for sucrose inversion was studied many years ago as a means for measuring acidity, half a century later, we now find the sugar industry employing the catalytic activity of ion exchange resins for producing invert sugar sirups from sucrose containing liquors.

During the past half century, catalysis by means of ion exchange resins evolved slowly and its progress followed that made generally in the field of heterogeneous catalysis. In many instances, the role of ion exchange in heterogeneous catalysis was primarily one of rationalizing the function and possible mechanism of such heterogeneous catalysts as the aluminas, carbons, and the various alumino-silicates. In other words, the ion exchange properties of the alumino-silicate, carbon, and the alumina surfaces were found to account for the catalytic properties of these solids.

The petrochemical industry is probably one of the largest consumers of ion exchangers as catalysts . . . in the use of the natural clays, synthetic alumino-silicates, and the synthetic zeolites in the cracking of petroleum and for various hydroforming and hydrocracking operations in the manufacturing of gasoline and other petroleum by-products. The current large-scale usage of the alumino-silicates as catalysts in petrochemical operations has led to the amassing of much information relating the ion exchange properties of these materials with their catalytic properties.

The successful use of the inorganic ion exchangers has led to the use of ion exchange resins as catalysts because these materials offered opportunities to achieve catalytic properties that could not be realized with the inorganic ion exchangers. This historical development parallels the transition from the inorganic ion exchangers to the ion exchange resins for most ion exchange applications.

In selecting an ion exchange resin as a catalyst for a particular reaction, one usually is attempting to replace some soluble acid or base that has previously been employed in a homogeneously catalyzed reaction. This desire to consider an ion exchange resin over soluble acids or bases is dependent upon several basic advantages in employing ion exchange resins as catalysts in heterogeneously catalyzed systems. These advantages are based on (1) the fact that there are now available ion exchange resins whose acidities and basicities are equal in strength to soluble mineral acids and bases such as H_2SO_4 and NaOH and (2) the fact that these properties can be exploited in heterogeneous catalytic systems. The advantages of heterogeneous catalysis using ion exchange resins over the comparable homogeneously catalyzed systems using soluble acidic or basic catalysts are as follows:

1. The catalyst is readily separated from the product of the reaction and can be re-used many times.
2. The product of the reaction is not contaminated by the catalyst and therefore requires less or no further purification.
3. The ion exchange resin catalyzed system is usually more selective and results in less by-product formation with an increase in overall yields.
4. The ion exchange resin system is less corrosive than the comparable homogeneously catalyzed systems involving such acid catalysts as hydrochloric and sulfuric acids.

Although ion exchange resin catalysis does not involve any ion exchange reactions, it is most interesting to note that many basic considerations involving the use of ion exchange resins as catalysts are quite similar to those involving the use of the same products for reactions involving the exchange of ions. For example, the overall rate mechanisms for both applications are diffusion-controlled reactions. Temperature limitations are also approximately the same. Further, in many respects, the engineering required for catalysis and ion exchange are also quite similar. With respect to engineering considerations, as in the case of ion exchange applications, the catalyst systems can be conducted in batch-type and columnar-type reactors. Although batch-type systems are but rarely used for ion exchange operations because of equilibrium considerations, batch-type reactors (or stirred reactors) are commonly employed in catalysis since the equilibrium nature of most catalytic reactions is such that there exists but little advantage for columnar over batch operations.

General Considerations

The major problems with which one is concerned in the application of ion exchange resins as catalysts are (1) the selection of the proper ion exchange resin and (2) the optimum conditions for their use. These problems, however, are not unique for ion exchange resin catalyst systems. They are encountered in all areas of catalysis. In many respects, the choice of an ion exchange resin as the catalyst for a particular reaction depends upon criteria not unlike those employed for selecting an ion exchange resin for ion exchange operations. Although there are some notable exceptions, ion exchange catalysis is primarily limited to those reactions that are catalyzed by either acids or bases. In this respect, one first considers the use of an ion exchange resin as a catalyst after having available to him the knowledge that the reaction he wishes to catalyze can be catalyzed by either an acid or a base. With this basic information, the choice between an anion exchange resin and a cation exchange resin becomes obvious since the former in the hydroxide or free amine state is a base and the latter in the hydrogen form is an acid.

Having made a choice between an anion exchanger and cation exchange resin, one can narrow the choice to a further degree. For example, since there are available both weak and strong acid ion exchange resins as well as weak and strong base anion exchange resins, one can select the cation or anion exchange resin that corresponds to the acid or base strength desired for the catalytic reaction.

The above-noted reasoning still does not result in the selection of the optimum ion exchange resin. Further consideration must be given to such factors as particle size, crosslinkage, and pore structure.

With respect to these factors, one must carefully consider the nature of the reaction. If the reaction that is to be catalyzed is to be conducted in an aqueous solution or a solution of high dielectric strength (highly polar medium such as methyl alcohol), one will probably **not** require a macroreticular ion exchange resin and will probably find the microreticular ion exchange resin (gel-type ion exchanger) to be the preferred catalyst. To zero in on crosslinkage and particle size of the ion exchange resin will probably require some experimentation. However, since diffusion plays an important role in ion exchange catalysis, one may relate these variables with the molecular weight of the reactants and product of the reaction. For example, if the reactants and products are of a high molecular weight, an ion exchange resin catalyst of low crosslinkage and small particle size will be preferred. This reasoning does not imply that larger particles of a more highly crosslinked ion exchange resin would be ineffective. It would only be less efficient and would require a higher temperature to obtain the same efficiency. Tables 1 and 2 describe the effects of particle size, temperature, and crosslinkage on the catalytic efficiency of a gel-type (microreticular) sulfonic acid ion exchange resin for the inversion of sucrose in water.

Should one be considering the use of an ion exchange resin for catalyzing a reaction in which the medium (gas or liquid) is non-polar (low dielectric constant), one must then select the proper macroreticular ion exchange resin. The choice of a macroreticular ion exchange resin for catalyzing reactions in non-polar media is analogous to the need for the use of similar ion exchange resins for ion exchange operations in similar media. This topic was discussed in detail in the previous issue of AMBER-HI-LITES (Issue No. 126). Table 3 describes the difference in catalytic activity between a macroreticular and microreticular ion exchange resin in a medium of low dielectric strength. The data require little explanation. Because of the diffusion-controlled nature of ion exchange catalyzed reactions and the low diffusion rates encountered with microreticular ion exchange resins in media of low dielectric strength, one requires the surface areas and pore structures of the macroreticular ion exchange resins to obtain the necessary overall catalytic activities.

The next issue of AMBER-HI-LITES will describe in detail the use of the Amberlite and Amberlyst ion exchange resins for the catalysis of specific and typical reactions.

TABLE 1

Effect of Particle Size and Temperature on Catalysis(1) of a Microreticular Sulfonic Acid Cation Exchange Resin (Amberlite IR-120)

Particle Size, mm.	0.91	0.32	0.16
Temperature, °C.		**Catalyst Efficiency**	
30	0.32	0.45	0.48
40	0.60	0.42	1.10
50	1.10	1.80	2.15
70	2.80	4.80	5.80

(1) Esterification of ethyl alcohol and acetic acid.

TABLE 2

Effect of Porosity and Functionality of Microreticular Cation Exchange Resin on Catalysis of Sucrose Inversion

Functionality	Crosslinking %	Reaction Rate Constant X104 25° C.	50° C.	75° C.
RSO_3H	1	7.6	100	—
RSO_3H	4	5.2	110	—
RSO_3H	10	0.7	26	117
RSO_3H	15	—	3	49
RSO_3H	20	—	0.7	23
RCOOH	2	—	—	50
RCOOH	5	—	—	9

TABLE 3

Comparison of Catalytic Activities of Macroreticular and Microreticular Sulfonic Acid Cation Exchange Resins for Esterification Reaction (Methacrylic Acid + Isobutylene at 0° C.)

Reaction Time (Hours)	Per Cent Conversion Amberlyst 15(1)	Amberlite IR-120(2)
1	17	0
2	32	0
3	42	0
5	53	0
6	57	0
7	59	0
24	—	5 (25° C)

(1) Macroreticular
(2) Microreticular

Errata

AMBER-HI-LITES No. 126

In Table 2 of the previous issue of AMBER-HI-LITES, Amberlite IRA-938 and Amberlite IRA-401 were erroneously designated as *cation* exchange resins. They should be designated as *anion* exchange resins.

Recent Literature Items

Health and Soft Water

During the past several years, there have been various "reports" linking the incidence of various diseases with soft water. It is, of course, well-known that various diseases are water-borne and that animals and humans have been poisoned by the presence of various toxic substances in water supplies. On the other hand, many irresponsible claims that certain water treatment practices are injurious to health are totally unsubstantiated. Such reports include citing the relationship between cardiovascular disorders and soft water. A recent report by Water Conditioning Association International (No. 108/71-December 29, 1971) reviews this totally unsubstantiated claim and cites the following quotations from scientific and medical reports:

1. *Illinois Medical Journal*
   "A research team of nationally recognized scientists has concluded that there is no supportive evidence to link soft water as a cause in cardiovascular disease.

   Contrary speculations of a causal relationship between soft water and heart ailments were branded by the committee as unfounded."

   "The Panel has concluded on the basis of available data that no causal relationship has been established between the total dissolved inorganic constituents of drinking water and cardiovascular disease. It is abundantly evident that the minor constituents of food, water and the air are capable of influencing human physiology most profoundly. Well known examples include iron in anemia, iodine in goiter, and fluorine in tooth decay. The concentration of inorganic constituents is much greater in foods than in water, but the sum total of the constituents makes all sources important."
2. *T. W. Anderson—Proc. Fifth International Water Quality Symposium* (P. 92)
   "In conclusion, I would suggest that we all try to avoid becoming emotionally committed, one way or the other, to the water factor heart disease debate, and have the patience to wait until all the evidence is in. Personally, I believe that some sort of water factor will eventually be identified, but until it is and until we know how it works and in what quantity it needs to be added or removed, it would be rash to abandon the present well-tried methods of water selection, treatment and delivery."

Their medical and scientific reports require no further comment.

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CATALYSIS WITH ION EXCHANGE RESINS (continued)

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In two previous issues of AMBER-HI-LITES (Nos. 127 and 128), the writer reviewed the basic principles of the phenomenon of catalysis and the use of ion exchange resins as catalysts. In general it was noted that, by their very nature, ion exchange resins are effective catalysts for those reactions that can be catalyzed by either acids or bases. Although these reactions can also be catalyzed homogeneously by soluble acids and bases, it was further noted that there were several basic advantages to the use of ion exchange resins as heterogeneous catalysts. The advantages cited are as follows:

1. The ion exchange resin catalyst is readily separated from the product of the reaction.
2. The product of the reaction is not contaminated by the ion exchange resin catalyst and therefore requires little or no further purification.
3. The ion exchange resin catalyzed system is usually more selective than the homogeneously catalyzed systems.
4. The ion exchange resin catalyst usually results in higher yields and less by-product formation.
5. The ion exchange resin catalyst can be reused many times.
6. The ion exchange resin system is less corrosive than the comparable homogeneously catalyzed systems involving such acids as hydrochloric and sulfuric acids.
7. The ion exchange resin heterogeneously catalyzed reactions are usually more readily controlled than the homogeneously catalyzed reactions.
8. The reaction products of the ion exchange resin catalyzed reactions do not require neutralization as is normally required with the use of soluble acid or base catalysts.
9. In many instances, the use of the heterogeneous ion exchange resin catalysts results in lower overall costs than those encountered with soluble catalysts.
10. Because they are more readily controlled, the ion exchange resin heterogeneously catalyzed reactions are generally considered safer than the corresponding homogeneously catalyzed reactions.

Although ion exchange resins in either the hydrogen form (cation exchangers) or the hydroxide form (anion exchangers) may be used for any acid or base catalyzed reaction, they are generally considered ideal catalysts for reactions such as hydrolysis, condensation, addition, esterification, dehydrohalogenation, dehydration, ammonolysis, alcoholysis, ester interchange, and alkylation reactions. The major disadvantage to the use of ion exchange resins as heterogeneous catalysts concerns their overall temperature stability. As is the case for general ion exchange resin operations, cation exchange resin catalysts are limited to temperatures below 125°C and anion exchange resin catalysts to temperatures below 60°C. For short periods of time, the maximum temperatures may be increased to 150°C and 90°C, respectively.

The previous two issues of AMBER-HI-LITES on catalysis were general in nature and were essentially void of procedural details. This issue and subsequent issues will attempt to inform the reader of such details.

General Laboratory Procedures

As in the case of conventional ion exchange systems, ion exchange resin catalyzed reactions may be conducted under batch conditions or under columnar conditions. These procedures will be outlined in the following paragraphs.

The simple batch process will satisfy all requirements for the preparative application in the laboratory. The ion exchanger is added to the starting substances in a regular flask containing some stirring arrangements. A three-neck flask is commonly used. One should wait for the adjustment of the equilibrium. Boiling under a reflux is indicated in most cases when the reaction requires a higher than normal temperature. Reactions under pressure are carried out in an autoclave. It is necessary in all cases to test the stability of the exchanger. The exchanger is separated by decantation, or better by filtration, after the reaction is finished. This discontinuous or batch method can be carried out in different ways; for instance by recirculating the liquid constantly through a bed of exchanger or by using a Soxhlet extraction apparatus. The batch process can be converted into a continuous one by equipping the reaction vessel with an overflow and by letting the starting materials enter continuously. It is necessary in this case to have good mixing.

The simplest arrangement for a continuous process consist of a column filled with the ion exchange resin as is commonly done for most ion exchange processes. The starting materials filter through the exchanger, and the reaction products appear in the effluent. This method can be adjusted to most reactions and a large number of continuous industrial processes are based upon this principle. The processes are convenient and give products of high purity at very high yields.

Ion exchange resin catalysts are probably not exhausted by these procedures. In principle, it should be possible to use ion exchange resins in this manner for any reaction which is catalyzed by an ion. Depending upon the nature of the reaction, one may use either weak or strong acid cation exchange resins for acid catalyzed reactions. For base catalyzed reactions one may use either strong or weak base anion exchangers.

Specific Ion Exchange Resin Catalysis Procedures

The following detailed ion exchange resin catalyzed reaction procedures are typical of the major applications now in use or are under active consideration for commercial use:

Epoxidation of Methyl Oleate

Prepare a mixture of 29.6 g. (0.10 mole) of technical methyl oleate (iodine number 81.75), 18.0 g. of the hydrogen form of a sulfonic acid cation exchange resin such as AMBERLITE IR-120 (16-20 mesh) treated with 2.75 g. acetic acid, and 0.55 g. of glacial acetic (0.055 mole total acetic acid) in a 100 ml. vessel equipped with a mechanical stirrer, thermometer, and dropping funnel. While the mixture is being stirred vigorously, add 7.48 g. (0.11 mole) of 50% hydrogen peroxide so that the temperature reaches 60°C for 2 hours, first with intermittent cooling by ice-water until the exotherm subsides and then by warming in a water bath. At the end of this time, cool the mixture in ice, and remove the resin by vacuum filtration. Collect the filtrate containing the product in 100 ml. of cold 1% NaCl solution. Separate the oily product layer, and then wash with 100 ml. portions of 1% NaCl solution.

Care should be taken to completely exclude traces of certain polyvalent metallic ions such as iron, copper, manganese, etc., since, in the presence of peroxide, degradation of the ion exchanger will be accelerated.

Alkylation of Phenol(1)

a. Place phenol (94 parts), diisobutylene (124 parts), and the dehydrated acid form of AMBERLYST 15 (dry(2)) catalyst (0.75 part) in a dry 500-ml. 3-necked flask and heat at 70° to 75° under an atmosphere of dry nitrogen. Remove the catalyst by filtering the hot reaction mixture and distill the p-tert-octylphenol (B.P. 140° to 180°/20 mm.) from the reaction mixture under reduced pressure. A yield of 57 percent is obtainable in one hour.

b. Mix phenol (18.8 parts), ether (20 parts by volume), and AMBERLYST 15 (2 parts) in a pressure vessel. Cool the pressure vessel to −10°C. and add isobutylene (22.4 parts) as a liquid. Close the pressure vessel and agitate for 3 hours. Considerable heat is evolved as the mixture warms and the reaction is essentially complete after 3 hours. The pressure vessel is cooled and vented, and the reaction mixture is filtered. The filtrate is stripped of solvent and distilled under pressure to get p-tert-butylphenol (18.9 parts, 63% conversion, B.P. 160°-167° (75 mm.)) and recovered phenol, 5.8 parts, 31%. Thus, the yield of p-tert-butylphenol based on phenol consumed is 93% of the theoretical.

Decomposition of Cumene Hydroperoxide to Phenol and Acetone

A mixture of acetone (25 parts) and AMBERLYST 15 (2 parts) are heated to reflux and a 70% cumene hydroperoxide solution in cumene (44 parts) is added dropwise under reflux. The addition requires 3.5 hours. Scans of the infrared spectrum from time to time in the course of the addition show that the hydroperoxide peak at 12.0 microns is absent. This implies that the conversion of the hydroperoxide to phenol and acetone takes place as rapidly as the addition is carried out. The catalyst is separated by filtration and the reaction mixture is distilled to give acetone, cumene, 11.5 parts, and phenol, 13.5 parts, B.P. 180° to 184°. A typical yield of phenol is 17.6 parts, 93% based on cumene hydroperoxide initially present.

Ester Formation

A mixture of methacrylic acid (86 parts) and dry AMBERLYST 15 (10 parts) are charged to a reactor and allowed to stand at room temperature overnight. The reactor is cooled and isobutylene (56 parts) is added to the stirred mixture as a liquid. During the 10-minute period required for this addition, the reactor and its contents are cooled to −5°. Thereafter, the temperature is maintained at 0°-1° by cooling the reactor in an ice-bath; samples are removed from time to time so that the progress of the reaction can be followed throughout its course. Unreacted isobutylene is allowed to evaporate from these samples and the residue is assayed (1) by titration with N/10 sodium hydroxide solution to determine unreacted methacrylic acid, and (2) by means of gas chromatography. The course of the reaction is summarized as follows:

Reaction Time (hours)	Percent Methacrylic Acid	Percent Crude Ester	Percent Conversion
1.	52.5	47.5	32.7
2.	38.3	61.7	47.1
3.	31.8	68.2	. . . .
4.5.	25.3	74.7	. . . .
6.	23.2	76.8	. . . .
7.	23.5	76.5	64.2

Quantitative gas chromatography of the crude product shows that in addition to methacrylic acid

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(1) U. S. Patent 3,037,052 (May 29, 1962)

(2) Dried at 110°C under reduced pressure.

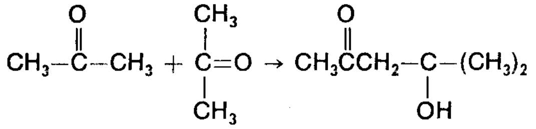
and tertiary butyl methacrylate, small amounts of other products are also obtained. Among these are diisobutylene (4.2%), triisobutylene (1.9%), and tertiary butyl alcohol (0.6%).

When a sample of the reaction mixture is allowed to stand in contact with the catalyst at room temperature overnight, little or no tertiary butyl methacrylate can be isolated because complete reversion of any ester formed has occurred owing to the prolonged contact with the catalyst at room temperature. This reversion is a result of the equilibrium nature of the reaction. Quantitative recovery of methacrylic acid is observed and all of the isobutylene initially fed can be accounted for as a mixture of di-, tri-, and tetraisobutylenes. It may be seen from the data that the addition of methacrylic acid to isobutylene is very rapid in the presence of this catalyst and that equilibrium is reached at 0°C about five hours after the reactants are initially combined.

All of the above-noted procedures pertain to the use of the hydrogen form of sulfonic acid cation exchange resins as catalysts. The literature, particularly the patent literature, is abound with such examples. With respect to the use of anion exchange resins as catalysts, the literature is less bountiful. The lack of information on the use of anion exchange resins is primarily a result of the lesser thermal stability of these exchangers as compared to the strongly acidic, sulfonic acid cation exchange resins. Because of the greater thermal stability of the weak base anion exchange resins, these anion exchangers seem to be preferred as catalysts over the strong base anion exchange resins.

Aldol Condensation

The aldol condensation of acetone,

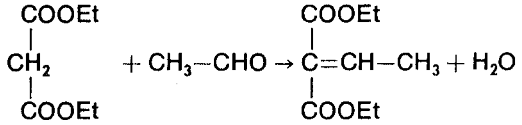


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + \underset{CH_3}{\overset{CH_3}{C}}=O \rightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2-\underset{OH}{C}-(CH_3)_2$$

can be readily catalyzed to form diacetone alcohol at the boiling point (56°C) of acetone using a Soxhlet extractor with the hydroxide form of a strong base anion exchanger (AMBERLITE IRA-400) in the thimble. The reaction takes place as the acetone vapors pass through the catalyst in the thimble and the diacetone alcohol is collected in the flask below. The reaction proceeds quite readily and is completed within an hour or so.

Knoevenagel Reaction

In the Knoevenagel reaction, the reaction between esters and aldehydes,



$$\underset{COOEt}{\overset{COOEt}{CH_2}} + CH_3-CHO \rightarrow \underset{COOEt}{\overset{COOEt}{C}}=CH-CH_3 + H_2O$$

can be readily catalyzed by macroreticular weak base anion exchange resins such as AMBERLYST A-21 in either the free base or acetate forms. This reaction may be conducted by refluxing the mixture in benzene solution which serves the double purpose of controlling the temperature (ca 80°C) and removing the water of reaction as an azeotrope. The reaction is essentially complete within an hour or so. The AMBERLYST A-21 may be used over and over again without significant loss in activity.

There are instances, such as in the case of hydrolysis, where both anion and cation exchange resins will catalyze reactions. In such cases, the choice will depend upon the required temperatures for the two systems and the relative stabilities and frequency of rejuvenation of the anion and cation exchange resins. There are also instances where a Monobed system or a mixture of an anion and cation exchange resin is advisable. Such mixtures avoid the side reactions encountered due to the "sloughage" of traces of soluble acids and bases from the ion exchange resins or the acid and base generated by exchange reactions involving the hydrogen form of the cation exchange resin (and the hydroxide form of the anion exchange resins) with electrolyte impurities in the reaction mixture.

The general nature of heterogeneous catalysis with ion exchange resins, as well as other catalysts, is such that the design of installations cannot be attempted without prior experimentation and study. As in the area of water treatment, as more and more experience in the use of ion exchange resins as catalysts is amassed, the extensive need for prior experimentation and pilot plant studies will diminish. It is unlikely, however, that it will reach the state where catalysis plants will be designed without prior experimentation as is now the state-of-the art in water treatment.

Although essentially in its infancy, ion exchange resin catalysis is a "going proposition" and several large installations have been operating successfully in various areas of the world. Future issues of AMBER-HI-LITES will present details of these installations.

Recent Literature Items

Ion Exchange Resin Catalysis of Direct Hydration of Olefins to form Isopropyl Alcohol.

A recent article (W. Neier and J. Woellner, Chem. Tech. p. 95, Feb. 1973) describes the design and operation of a large plant (Deutoche Texaco AG., Hamburg, W. Germany) devoted to the synthesis of isopropanol via the hydration of propylene using a sulfonic acid cation exchange resin (such as AMBERLYST 15) as the catalyst.

The plant consists of several reactors in parallel of the following design, shown in Figure 1.

The mixture of liquid water and gaseous propylene is fed to the top of the reactors. Both phases are fed to the reactor simultaneously and in the same direction. The process water is recycled from the alcohol purification section but is first deionized by means of ion exchange. Some of the water is cooled (6)* used to quench the reactor and the bulk metered (7) into the reactor. Propylene is pumped from a pressure container to an intermediate vessel (12) through a pump (13) and then into the process water stream and fed to the reactors (10) (4 ion exchange resin catalyst beds) as a vapor/liquid mixture. The aqueous alcohol and residual gas are passed to a high pressure vapor/liquid separator (14) and via a heat exchanger (8) to a low pressure separator. From there the crude isopropyl alcohol is sent to a distillation plant for purification. The optimum water/propylene molar ratio was found to be 12.5-15.0/1. A temperature range of 130°-150°C and a pressure of 60-100 atmospheres were found to be most effective. Under optimum conditions a conversion of the propylene was found to be 75% per pass.

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* These numbers refer to Figure 1.

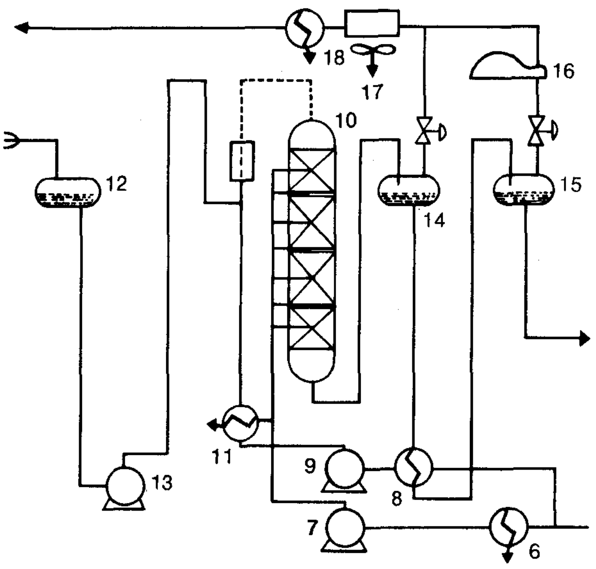


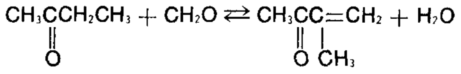
FIGURE 1—Schematic sketch of reactor for hydration of propylene to isopropyl alcohol.

The authors cite the following advantages of the ion exchange catalyzed system over the older catalytic system based upon the use of sulfuric acid.

1. Reduction of corrosive damage. The substantial damage by corrosion during reconcentration of sulfuric acid in the submerged burner plant will be eliminated.
2. Reduction in energy costs, partly resulting from eliminating the re-concentration of sulfuric acid.
3. Reduction of the amount of high COD waste water.
4. Reduction of air pollution. Small amounts of SO_2 and organic sulfur compounds are present in waste gases emitted during re-concentration of the acid.

The same authors note that they have successfully operated two other plants using ion exchange resins as catalysts. These plants involve the following two reactions:

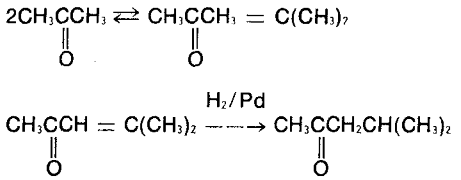
(a) Synthesis of methyl-isopropyl-ketone from methyl-ethyl-ketone and formalin



$$CH_3\underset{\overset{\|}{O}}{C}CH_2CH_3 + CH_2O \rightleftarrows CH_3\underset{\overset{\|}{O}}{C}\underset{\overset{|}{CH_3}}{C}{=}CH_2 + H_2O$$

(DBP 1,233,848; 1,198,814)

(b) Synthesis of methyl-isobutyl-ketone from acetone on a palladium-loaded cation exchange resin



$$2CH_3\underset{\overset{\|}{O}}{C}CH_3 \rightleftarrows CH_3\underset{\overset{\|}{O}}{C}CH_3 = C(CH_3)_2$$

$$CH_3\underset{\overset{\|}{O}}{C}CH = C(CH_3)_2 \xrightarrow{H_2/Pd} CH_3\underset{\overset{\|}{O}}{C}CH_2CH(CH_3)_2$$

(DBP 1,260,454; 1,193,931; 1,238,453; US 3,405,178; US 3,574,763.)

This article is quite timely since it refers to the successful operation of three large plants based upon the use of ion exchange resins as catalysts.

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amber-hi-lites

In the previous issue of AMBER-HI-LITES, the author introduced the topic of catalysis and described the general use of ion exchange resins as catalysts or catalytic agents. In general, it was noted that, by their very nature as acids and bases when in the hydrogen or hydroxide forms, ion exchange resins are used primarily for those reactions that heretofore were catalyzed by either soluble acids or bases. It was further noted that employing ion exchange resins as heterogeneous catalysts offered several advantages over the reactions homogeneously catalyzed with soluble acids and bases such as hydrochloric acid and sodium hydroxide. For example, the catalyst is readily separated and recovered by simple filtration from the reaction mixture and thereby does not contaminate the product. In many instances further purification of the product is avoided or minimized.

Properties of Amberlite and Amberlyst ion exchange resins commonly used as catalysts are summarized in Tables 1 and 2. Ion exchange resins having a macroreticular structure are preferred over the microreticular or gel-type ion exchange resins for many catalytic reactions, especially those carried out in nonpolar media. However, for reactions catalyzed in aqueous or polar liquids, it is common to find the gel-type ion exchange resins to be better suited than the porous, high-surface-area, macroreticular ion exchange resins.

TABLE 1 Properties of Microreticular (Gel-Type) Amberlite Ion Exchange Resin Catalysts
(All products, except where specified, 20-50 mesh)

Ion Exchange Resin	Skeletal Structure	Ionic Functionality	Crosslinkage, % DVB	Moisture Content	Ion Exchange Capacity meq/g	Ion Exchange Capacity meq/ml	Typical Catalytic Applications
Cation Exchange Resins							
Amberlite IR-118(a)	Styrene-DVB	RSO_3H	4-5	58	5.0	1.5	Sucrose Inversion, Esterification
Amberlite IRF-66(H) (100-325 mesh)	Styrene-DVB	RSO_3H	8	46	5.0	1.9	Epoxidation
Amberlite IR-120(a)	Styrene-DVB	RSO_3H	8	46	5.0	1.9	Esterification, Epoxidation
Amberlite IR-124	Styrene-DVB	RSO_3H	12	39	5.0	2.2	Hydration of olefins
Amberlite IRC-84	Acrylate-DVB	RCOOH		46	10.5	3.5	Partial sucrose inversion
Anion Exchange Resins							
Amberlite IRA-400	Styrene-DVB	Quaternary		45	3.8	1.4	Aldol Condensation
Amberlite IR-45	Styrene-DVB	Primary & Secondary		43	5.8	1.9	Knoevenagel Reaction
Amberlite IRA-68	Acrylate-DVB	Tertiary amine		60	5.6	1.6	Aldol Condensation

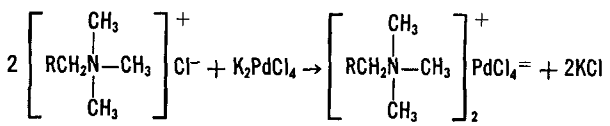
(a) Available in low iron content (<15 ppm).

TABLE 2 Properties of Macroreticular Amberlyst Ion Exchange Resin Catalysts
(20-50 mesh)

Ion Exchange Resin	*Skeletal Structure*	*Ionic Functionality*	Porosity, %	Surface Area, meter²/g	Ion Exchange Capacity meq/g	Ion Exchange Capacity meg/ml	Typical Catalytic Applications
Cation Exchange Resins							
Amberlyst 15	Styrene-DVB	RSO_3H	32	45	4.6	1.8	Alkylation
Amberlyst XN-1005	Styrene-DVB	RSO_3H	42	130	3.4	1.5	Anhydrous Esterification
Amberlyst XN-1010	Styrene-DVB	RSO_3H	47	570	3.3	1.0	Transvinylation
Amberlyst XN-1011(b)	Styrene-DVB	RSO_3H	24	28	4.2	1.2	High Temperature Hydration
Anion Exchange Resins							
Amberlyst A-26	Styrene-DVB	Quaternary	27	28	4.4	1.0	Aldol Condensation
Amberlyst A-27	Styrene-DVB	Quaternary	51	65	2.6	0.7	Aldol Condensation
Amberlyst A-21	Styrene-DVB	Tertiary Amine	48	25	4.8	1.3	Nitrile hydrolysis

(b) Amberlite XN-1011 is a newly developed macroreticular cation exchange resin for catalytic and non-aqueous applications requiring a resin with unusual thermal stability.

Although Amberlite and Amberlyst ion exchange resins are usually employed in the hydrogen and hydroxide forms as acid and base catalysts, their structures are unusually suited as substrates for various metals and metallic complexes to form unique selective catalysts. For example, the $\mathrm{PdCl_4^=}$ salt of the macroreticular quaternary ammonium anion exchange resin can be formed by means of the following reaction:



$$2\left[\mathrm{RCH_2\overset{CH_3}{\underset{CH_3}{N}}-CH_3}\right]^+\mathrm{Cl^-} + \mathrm{K_2PdCl_4} \rightarrow \left[\mathrm{RCH_2\overset{CH_3}{\underset{CH_3}{N}}-CH_3}\right]^+_2\mathrm{PdCl_4^=} + 2\mathrm{KCl}$$

Similarly one can form the $\mathrm{Pt(NH_3)_4^{++}}$ form of the macroreticular, sulfonic acid cation exchange resin, Amberlyst 15, as follows:

$$\mathrm{2RSO_3H + Pt(NH_3)_4Cl_2 \rightarrow (RSO_3)_2Pt(NH_3)_4 + 2\ HCl.}$$

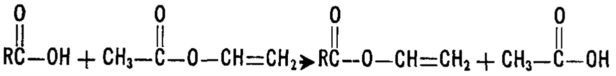
Each of these catalysts is useful for those reactions requiring CO and H_2 as reactants. Various mercury derivatives of the macroreticular sulfonic acid cation exchange resin, Amberlyst 15, can be obtained by reaction with mercuric acetate, $\mathrm{Hg(OAc)_2}$, according to the following stoichiometry:

$$\mathrm{2R\text{-}SO_3H + Hg(OAc)_2 \xrightarrow{25^\circ C} (R\text{-}SO_3)_2Hg + 2HOAc}$$

$$\mathrm{R\text{-}SO_3H + Hg(OAc)_2 + H_2O \xrightarrow{60^\circ C} R\text{-}SO_3\text{-}Hg(OH) + 2HOAc}$$

$$\mathrm{R\text{-}SO_3H + Hg(OAc)_2 \xrightarrow[HOAc]{60^\circ C} R\text{-}SO_3\text{-}Hg(OAc) + HOAc}$$

These mercury derivatives of Amberlyst 15 have been found to be excellent catalysts for the transvinylation of a large variety of carboxylic acids:

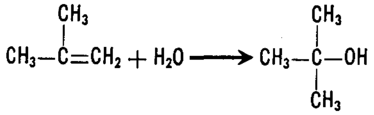


$$\mathrm{R\overset{O}{\overset{\|}{C}}-OH + CH_3-\overset{O}{\overset{\|}{C}}-O-CH{=}CH_2 \rightarrow R\overset{O}{\overset{\|}{C}}-O-CH{=}CH_2 + CH_3-\overset{O}{\overset{\|}{C}}-OH}$$

Acid Catalysis

Hydration

Amberlite IR-120 and Amberlite IR-124 have been used with excellent results for the hydration of isobutylene to form t-butyl alcohol at a temperature of about 90-100°C:



$$\mathrm{CH_3-\overset{CH_3}{\overset{|}{C}}{=}CH_2 + H_2O \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OH}$$

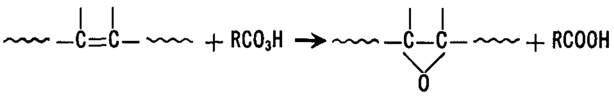
The same ion exchange resin catalysts can also function as dehydration catalysts.

Alkylation

Whereas the previous hydration reaction could be catalyzed effectively by a gel-type or microreticular ion exchange resin such as Amberlite IR-124, alkylation of aromatics such as toluene and phenol with reactants such as isobutylene or propylene require a macroreticular sulfonic acid catalyst such as Amberlyst 15 for efficient and effective operation. These reactions heretofore have been catalyzed homogeneously by BF_3 and H_2SO_4 and have required considerable rectification and purification steps to recover the desired alkylated product. When the Amberlyst 15 is employed as the catalyst, the "work-up" of the product requires but the "flashing off" of the unreacted low boiling reactants from the higher boiling alkylated aromatic. For example, nonyl and octyl phenols can now be produced quite simply in high purities and very economically, with the aid of Amberlyst 15 (U.S. Patent 3,027,052, May 29, 1962).

Epoxidation

The use of a sulfonic acid cation exchange resin such as Amberlite IR-120(H) for the epoxidation of natural fats and oils with various per-acids,

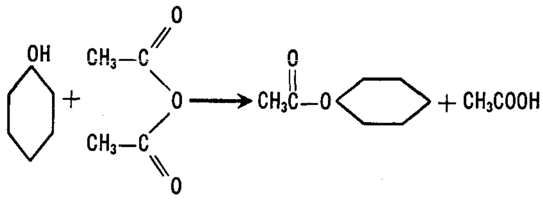


$$\sim\sim-\overset{|}{C}{=}\overset{|}{C}-\sim\sim + \mathrm{RCO_3H} \rightarrow \sim\sim-\underbrace{\overset{|}{C}-\overset{|}{C}}_{O}-\sim\sim + \mathrm{RCOOH}$$

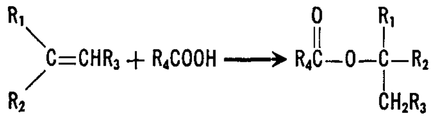
is now practiced widely throughout industry. The reaction is an example in which the gel-type sulfonic acid cation exchange resin, Amberlite IR-120, is preferred over the macroreticular sulfonic acid cation exchanger, Amberlyst 15. The pore structure of the latter actually retains the reactants and product for too long a period of time and thereby reduces the yield of epoxide and increases the degree of hydroxylation, an undesired side reaction.

Esterification

For the esterification of the lower-molecular-weight alcohols and organic acids, Amberlite IR-118 in the acid form is an excellent catalyst under reflux conditions. The same catalyst is also quite effective for the esterification of butyl oleate from butanol and oleic acid. For the formation of esters in anhydrous media, a macroreticular acid catalyst such as Amberlyst 15 is required. The preparation of phenyl acetate by reacting phenol and acetic anhydride is an example of esterification in anhydrous media:



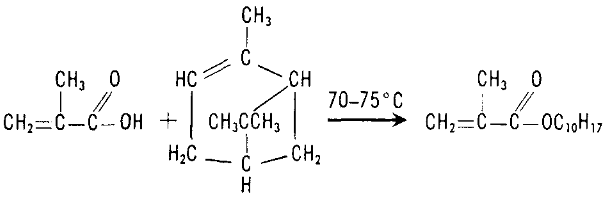
Amberlyst 15 is also an effective catalyst for forming esters by reacting a variety of olefins with various carboxylic acids:



$$\mathrm{{}^{R_1}_{R_2}{>}C{=}CHR_3 + R_4COOH \longrightarrow R_4\overset{O}{\overset{\|}{C}}-O-\overset{R_1}{\underset{CH_2R_3}{C}}-R_2}$$

For example, Amberlyst 15 is an effective catalyst for reacting methacrylic acid and isobutylene at temperatures as low as 0°C.

The effect of surface area on the catalytic activity of a series of macroreticular sulfonic acid cation exchange resins can be illustrated using the reaction between methacrylic acid and pinene:



Amberlyst XN-1010 is considerably more effective than Amberlyst XN-1005 which in turn is more effective than Amberlyst 15. This order of reactivity follows the surface area variations for these Amberlyst resin catalysts as described in Table 2.

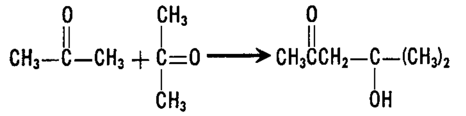
It would be beyond the scope of this article to describe in further detail the use of cation exchange resins as acid catalysts; however, summarized in Table 3 are those reactions that can be effectively catalyzed by Amberlyst 15 and other related sulfonic acid cation exchange resins.

Base Catalysis

Although most of the ion exchange resin catalyzed reactions studied over the years have been those that have been catalyzed by sulfonic acid cation exchange resins, as noted in the previous issue of AMBER-HI-LITES, there exist a modest number of reactions that are base-catalyzed by anion exchangers such as Amberlite IRA-400, a strong base gel-type material, and Amberlyst A-26, a macroreticular anion exchange resin.

Aldol Condensation

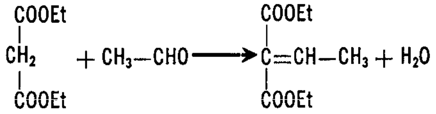
The condensation of various aldehydes can be readily catalyzed by various weak base and strong base anion exchange resins such as Amberlyst A-21 and Amberlyst A-26. For example, acetone can be condensed to form the diacetone alcohol:



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_3+\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}=O \longrightarrow CH_3\overset{\overset{O}{\|}}{C}CH_2-\underset{OH}{C}-(CH_3)_2$$

Knoevenagel Reaction

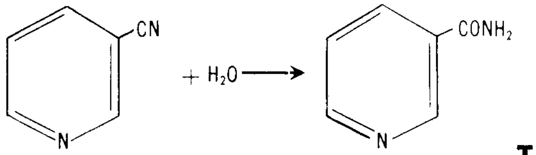
The Knoevenagel Reaction



$$\begin{matrix}COOEt\\|\\CH_2\\|\\COOEt\end{matrix} + CH_3-CHO \longrightarrow \begin{matrix}COOEt\\|\\C\\|\\COOEt\end{matrix}=CH-CH_3+H_2O$$

can be readily catalyzed by a weak base anion exchange resin such as Amberlyst A-21 in either the free base or acetate forms.

Other reactions catalyzed by anion exchange resins include (1) the conversion of nicotinonitrile to the amide (the intermediate of nicotinic acid)



and (2) cyanoethylation, the reaction of nitriles and alcohols:

$$ROH + CH_2{=}CH-CN \longrightarrow ROCH_2-CH_2-CN$$

Stability of Ion Exchange Resin Catalysts

Amberlite and Amberlyst ion exchange resins are stable under a wide range of conditions. However, their usefulness as catalysts is limited primarily by their thermal stabilities. In the case of the cation exchange resins, products such as Amberlite IR-120 and Amberlyst 15 exhibit reasonable lives as catalysts at temperatures up to 150°C. Amberlyst XN-1011 is unique with respect to thermal stability and exhibits a useful life at temperatures close to 175-200°C. The weak base anion exchangers such as Amberlyst A-21 are limited to temperatures below 100°C, and the strong base anion exchangers such as Amberlite IRA-400 and Amberlyst A-26 in the hydroxide form cannot be used for prolonged periods above 60°C.

Catalyst Rejuvenation

During repeated use of the hydroxide form of the anion exchange resins and the hydrogen form of the cation exchange resins as base and acid catalysts, the effectiveness of the catalyst may gradually diminish as the hydroxide and hydrogen ions are replaced by various ionic constituents present in the reaction mixtures. The effectiveness of such catalysts can be restored by regeneration of the anion exchange resin with alkali and of the cation exchange resin with acid as is the case with exhausted ion exchange resins used in deionization systems.

It is also possible that the ion exchange resin catalyst must be re-dried or dehydrated if they gradually adsorb water during repeated use. Drying can be accomplished with solvents followed by vacuum drying or by means of azeotropic distillation.

On occasion, the Amberlyst ion exchange resin catalyst may become deactivated as a result of a "build up" of polymeric "crud" formed as a by-product of the catalyzed reaction. In such instances, reactivation of the catalyst can be accomplished by treatment with an alkaline hypochlorite (0.5% NaOCl, 0.5% NaOH) solution followed by alkaline regeneration of the anion exchange resin or an acid regeneration of the cation exchanger.

In the case of cation exchange resins that are fouled with highly polymeric "crud", reactivation may require treatment with concentrated sulfuric acid at 90°-100°C for a period of 4-8 hours.

TABLE 3

**Summary of Reactions Catalyzed by
Amberlyst 15 and Related Amberlite Sulfonic Acid
Cation Exchange Resins**

Olefin Reactions	Reactions with Water Formation	Other Reactions
Isomerization	Etherification	Transesterification
Polymerization	Esterification of alcohols and phenols	Transetherification
Alkylation	Alkylation with alcohols	Decomposition of hydroperoxides
Hydration	Condensation of aldehydes	Von Pechmann Reaction
Esterification	Polymerization of alcohols	Lactone Formation
Acrylation		
Mercaptan Addition		

In concluding this series of AMBER-HI-LITES articles on catalysis by means of Amberlite and Amberlyst ion exchange resins, one cannot but help emphasize that these products represent an unusual group of catalysts with a considerable degree of versatility resulting from the large number of functional groups and physical structures available for optimum catalytic activity.

Recent Literature Items

Macroreticular, Polymeric Adsorbents

The concern over the pollution of our water resources by various industrial and municipal effluents has created many problems in our attempts to police our waterways and to develop unique analytical and abatement techniques. In previous issues of AMBER-HI-LITES, the properties of a series of macroreticular, polymeric adsorbents were described and their use in pollution control and abatement was postulated. A recent publication [Analytical Chemicals *44,* 139 (1972)] by Professor J. S. Fritz and his associates of the Department of Chemistry of Iowa State University, Ames, Iowa summarizes the results of a comprehensive study on the use of Amberlite XAD-2 and Amberlite XAD-7 (two macroreticular adsorbents) for separating, concentrating and identifying a host of typical organic pollutants.

Using both Amberlite XAD-2 and Amberlite XAD-7, Prof. Fritz and his associates have developed a method for extracting trace organic contaminants from potable water. They have demonstrated that Amberlite XAD-2 and Amberlite XAD-7 are capable of adsorbing weak organic acids and bases and neutral organic compounds *quantitatively* from water containing parts per billion to parts per million concentrations of the contaminants.

The following is a list of compounds that Prof. Fritz found could be effectively removed from water by either Amberlite XAD-2 or Amberlite XAD-7:

Methyl isobutyl ketone
n-Hexanol
Ethyl butyrate
Benzene
Naphthalene
Benzoic acid
Phenylenediamine
Phenol
2,4-Dimethylphenol
p-Nitrophenol
2-Methylphenol
Aniline
0-Cresol
Acenaphthylene
1-Methylnaphthalene
Methylindenes
Indene
Acenaphthene
2-2-Benzothiophene
Isopropylbenzene
Ethyl benzene
Naphthalene
2,3-Dihydroindene
Alkyl-2,3-dihydroindene
Alkyl benzothiophenes
Alkyl naphthalenes

The acidic components were desorbed with alkali and the basic components with acid. The neutral compounds were eluted with ether.

Although the work of Prof. Fritz and his associates was analytically oriented, it does point to the potential use of Amberlite macroreticular, polymeric adsorbents for pollution control.

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