Ion Exchange Resins as Catalysts

(Extracted from the Diaion Manuals pages 327 to 353)

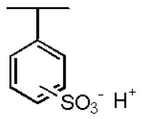
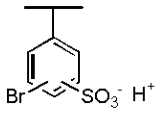
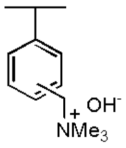
Chapter X Other Use

1. Applications as Catalysts

(1) Preface

IERs can be used as reaction catalysts of solid acids or solid bases as well as other acids or bases are used as catalysts. Although the primary application of IERs as catalysts have been only for esterification and hydrolysis of esters, they are used, with newly developed porous resins different from gel ones as a turning point, for other reactions in nonpolar solvents such as alkylation where IERs are difficult to be applied. Heat-resisting IERs, furthermore, have widened the applied fields. The representative reactions in the literatures including patents are summarized in Table X-1-1. Several reactions are industrialized with large amounts of IERs.

[Table X-1-1] IERs as Acid/Base Catalysts

IERs	Reactions
SACERs  	Hydrolysis Esterification Acetalization, Ketalization Cyclization Condensation Dehydration Decarbonation Hydrogenation Amidation
SBAERs 	Hydrolysis Dehalogenation Condensation Hydration Cyclization Esterification Acylation Phase Transfer Catalysts

(2) Characteristics

The advantages of IERs as catalyst are as follows:

i) Easiness to separate catalysts from reaction products:
It is easy to separate IERs from reaction systems in the batch operations, since they are solid acids or solid bases.

ii) Can be applied for continuous reactions and useful for rationalization of processes:
Continuous reactions with high productivity can be accomplished simply with the feed of starting materials into the reaction towers filled with IERs. Running costs are lower than normal acids or bases catalysts due to their superior availability to various reactions.

iii) Unnecessary to neutralize and to concentrate catalysts:
Treatments after reactions, e.g. neutralization and concentration, are unnecessary or easy, since IERs are solid.

iv) High selectivity with little byproducts:
IERs have high selectivity due to their molecular sieve effect.

v) Little erosion to facility materials:
IERs have less erosion than normal acids or bases and various facility materials can be applied. Thus, they are convenient to decrease the investment costs.

On the contrary, IERs have the following disadvantages:

i) Heat-resistance is lower than inorganic catalyst:
Standard IERs have inferior heat-stability to normal acids or bases and cannot be used at high temperatures since they are organic polymers. CERs are suitable for reaction at 100 ~120 °C and AERs can be used at 40 ~60 °C. They can be applied at higher temperatures when they are used for one-time use and for a short period. Heat-resistant CERs can also be used at higher temperatures.

ii) Reaction rates are low when reactants are polymers:
The reaction rates are slow when the reactants have large molecular sizes, since they are difficult to intraparticle diffusion due to IERs network structures.

(3) General property of IERs

Very many grades of IERs with different polymer matrix, degree of crosslinkage and functional group are on the market and thus they differ in catalyst-activity and reaction-selectivity. Thus, it is necessary to select proper grades of IERs depending on the reaction conditions, e.g. the polarity of the reaction systems, the molecular weights of the reactants and the reaction temperature. The points to consider when selecting proper grades of IERs are as follows:

1) Polymer Matrix

The polarity of the reaction systems is the most important factor to select the proper polymer matrix of IERs.

i) Gel-type IERs
Suitable for polar reaction systems, but not for non-polar ones

ii) Porous-type IERs
Suitable for polar reaction systems as well as gel-type IERs and efficient when the reactants are large in molecular size due to these IERs are porous

iii) Highly porous-type IERs
Suitable not only for polar solvents but also for non-polar ones

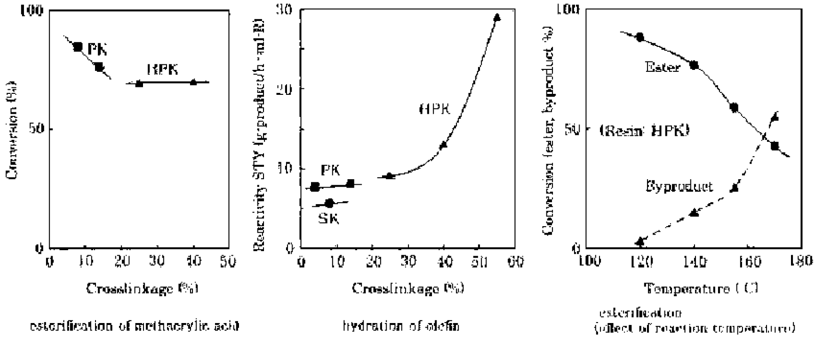
IERs with large ion-exchange capacity and of standard degree of crosslinkage are applied in polar reaction systems of rather small-size reactants. Those of low degree of crosslinkage are effective in reactions of large-size reactants. Gel-type IERs that have good mechanical strength are, in general, less active as catalysts than porous-type ones of the same degree of crosslinkage as gel-type. In non-polar reaction systems, only highly porous-type IERs are effective.

Please note: the laboratory testing to compare IERs with different polymer matrix of different degree of crosslinkage is recommended in advance of the final decision of the actual IER-grade.

Table X-1-2 and Fig.X-1-1 illustrate a selection model of CER grades and some examples of correlations between catalytic activity and IER-grades, respectively. Tables X-1-3 and X-1-4 also summarize the properties and the degree of swelling of the representative IER-grades, respectively.

[TableX-1-2] Selection CERs grades based on Reaction type

Solvents	Reaction	SK-series	PK-series	HPK/RCP-series
Aqueous	Esterification	←—	—→	
	Hydrolysis	←—	—→	
	Hydration		←—	—→
Nonaqueous	Alkylation			←→



esterification of methacrylic acid

hydration of olefin

esterification
(effect of reaction temperature)

[Fig.X-1-1] Catalytic activity vs. DIAION® -Grades

[TableX-1-3] Properties of representative IER-grades as catalysts

Grade	Type	Degree of Crosslinkage	Exchange Capacity	Particle Size (1180-425μm)	Moisture content	Apparent Density	Specific Surface Area	Pore Volume
			meq/mL	%	%	g/L	m^2/g	mL/g
SK104H	Gel-type	Low	>1.1	>99	63−69	730		
SK1BH	Gel-type	Normal	>1.6	>99	52−56	780		
PK208H	Porous type	Low	>1.0	>99	65−71	720		
PK216H	Porous type	Normal	>1.4	>99	53−57	750		
PK228H	Porous type	High	>1.6	>99	42−46	750	16	0.25
HPK25H	Highly Porous	Middle: Specific Surface Area	>1.2	>99	44−50		3	0.05
RCP145H	Highly Porous		>0.8	>99	60−70		50	0.40
RCP160H	〃		>1.5	>99	45−55			

[TableX-1-4] Degree of swelling of representative CER-grades as catalysts

Grade	Degree of Swelling (mL/g-dryR)							
	Water	Methanol	Ethanol	Iso-Propanol	Acetone	Dioxane	Dichloroethane	Toluene
SK104H	4.1	3.3	3.2	3.2	2.5	1.2	1.2	1.1
SK1BH	2.8	2.4	2.4	2.5	2.1	1.1	1.2	1.2
PK208H	4.6	3.7	3.6	3.6	2.5	1.2	1.1	1.1
PK216H	2.8	2.5	2.4	2.4	2.1	1.2	1.1	1.2
PK228H	2.2	2.1	1.6	1.6	1.4	1.2	1.2	1.2
HPK25H	2.5	2.4	2.5	2.5	2.4	2.3	2.0	2.0

2) Degree of Crosslinkage

The degree of crosslinkage of IER-grade is closely related with the size of its micro-pores. Thus, the reaction rates catalyzed by IER-grades with low degree of crosslinkage are high since such IERs have large-size micro-pores within which large reactants can diffuse. Another advantage of IER-grades with low degree of crosslinkage is their good heat-resistance. They, however, have disadvantages, e.g. with few active sites and poor oxidation resistance. Thus, the proper degree of crosslinkage should be decided from the point of the reaction properties.

3) Particle Size

The particle size of IER-grade is one of the most important factors to govern reaction rates as well as the micro-pore size, and reaction rates are fast with IERs of small particles. Still, the selection of such size should be decided in order to maintain stable operations, considering other reaction properties than reaction rates, e.g. viscosity of reaction systems, feed rate of reactants and side reactions.

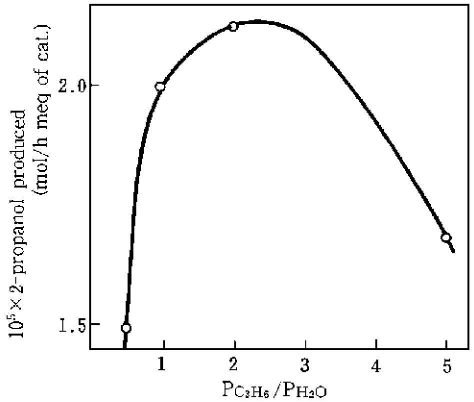
The rates of catalytic reactions are mostly governed by the diffusion rates of reactants within IER particles, because the reactions occur in the neighborhood of the functional groups of the IER. Thus, the smaller is its particle size the higher is the reaction rate. In the laboratory experiments to compare grades of IERs, the test samples should have the same particle size. Though the IERs of small particle size have another advantage of good mechanical strength, they may cause poor operativeness such as the increase of the pressure drop in the column.

4) Counter Ion

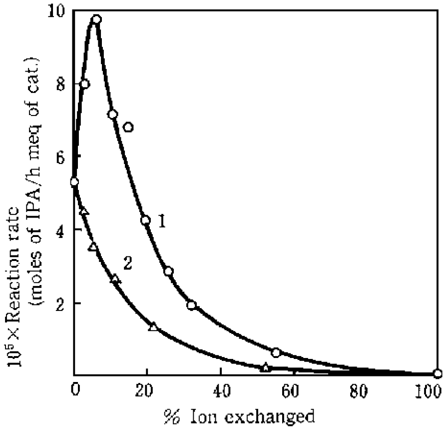
CERs and AERs are used as catalysts generally in H-form and OH-form, respectively. In some cases, they are used after partial neutralization or displacement by other ions in order to adjust their acidity or basicity or to heighten their affinity with reactants or reaction selectivity. Figures

X-1-2 and X-1-3 illustrate such an example of propanol formation. (128)

Please note: OH-form AERs tend to adsorb carbon dioxide and thus care must be taken in handling them in the atmosphere. In drying them, vacuum conditions are also recommended.



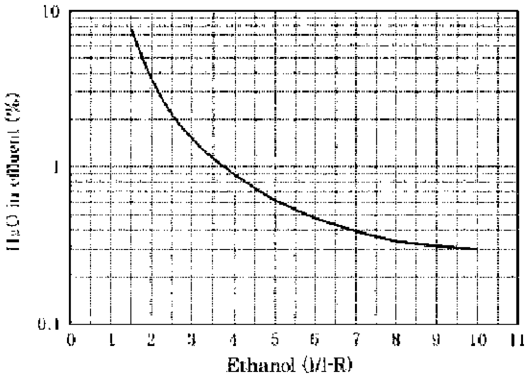
[Fig.X-1-2] Influence of mole ratio of propylene to water on 2-propanol production at 120℃.
Catalyst, SK1B; Flow rate 0.30mol/h (128)



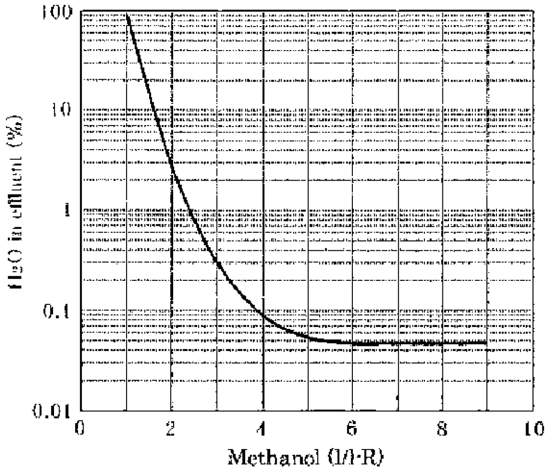
[Fig.X-1-3] Effect of partial ion exchange with Ag^+ or Na^+ on 2-propanol production at120℃.
1.— SO_3Ag resins, 2.— SO_3Na resins (128)

5) Product Form

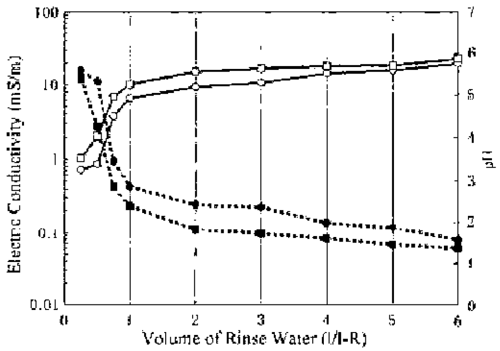
Most of product-IERs are on sale in wet state to avoid the deterioration of performance during the storage period. Hence, the water in product-IERs usually is displaced by alcohols in advance of the practical use. Figures X-1-4 and X-1-5 illustrate such displacement of water by anhydrous alcohol.



[Fig.X-1-4] Displacement of water in IERs by Ethanol

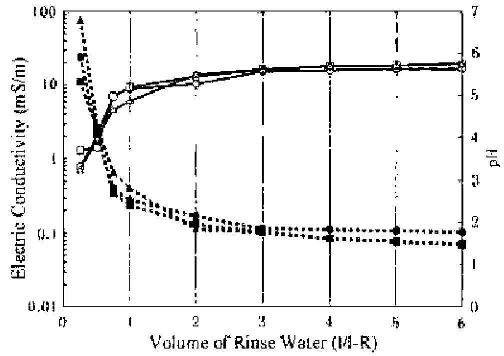


[Fig.X-1-5] Displacement of water in IERs by Methanol



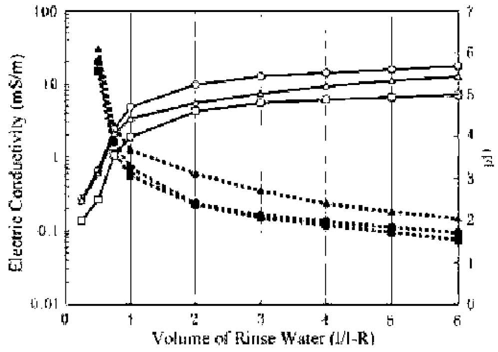
[Fig.X-1-6] Rinse example-1 of IERs with water: SK-series
Flow rate: SV=1
Temp.: room temp. (24 °C)
Rinse: Pure water
pH = 6.3
Electric Conductivity = 0.006mS/m

○● : SK1BH(Lot 1B303)
□■ : SK110H(Lot 1I302)
—— pH
------ Electric Conductivity



[Fig.X-1-7] Rinse example-2 of IERs with water: SK-series
Flow rate: SV=1
Temp.: room temp. (24 °C)
Rinse: Pure water
pH = 6.3
Electric Conductivity = 0.006mS/m

○● : SK104H(Lot 1H301)
□■ : SK104H(Lot 1H307)
△▲ : SK104H(Lot 1H313)
—— pH
------ Electric Conductivity

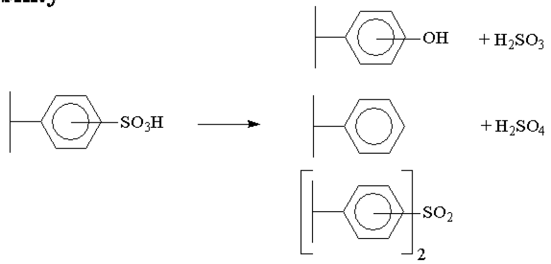


[Fig.X-1-8] Rinse example-3 of IERs with water: SK-series
Flow rate: SV=1
Temp.: room temp. (24 °C)
Rinse: Pure water
pH = 6.3
Electric Conductivity = 0.006mS/m

○● : PK208H(Lot 8H301)
□■ : SK208H(Lot 9F301)
△▲ : SK208H(Lot 9A301)
—— pH
------ Electric Conductivity

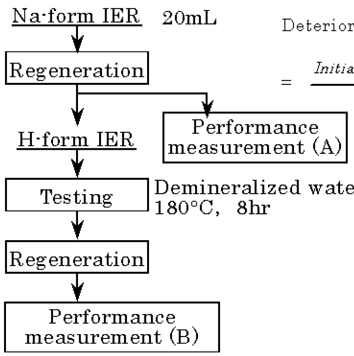
Some brand-new IERs are mingled with soluble polymers as impurities. Such polymers can be removed by rinses with water as illustrated in Figures X-1-6 through X-1-8.

(4) Heat Stability



[Fig.X-1-9] Decomposition mechanism of SACERs

IERs have limited heat-resisting property since they are organic polymers. Thus, they gradually deteriorate above a certain temperature due to the decomposition of their functional groups. Please note that SBAERs have poor heat stability particularly. The decomposition mechanism of SACERs is demonstrated in Fig.X-1-9.

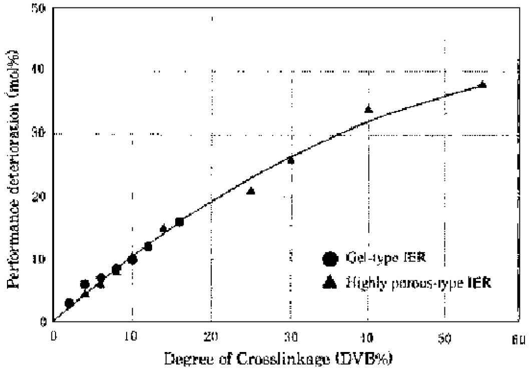


Demineralized water 20mL + IER in autoclave
180°C, 8hr

$$\text{Deterioration Rate(\%)} = \frac{(A)-(B)}{(A)} \times 100$$

$$= \frac{\textit{Initial Total Exchange Capacity} - \textit{Last Total Exchange Capacity}}{\textit{Initial Total Exchange Capacity}} \times 100$$

Fig.X-1-10 shows the experimental results of heat stability of IERs, the correlation between degrees of crosslinkage and deterioration rates, by the above-mentioned method. It lets us know that IERs of low crosslinkage have superior heat-resistance.



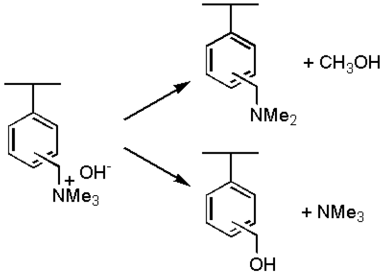
[Fig.X-1-10] Crosslinkage vs. Deterioration rate

Conditions IER: H-form Temp.: 180°C Time: 8h

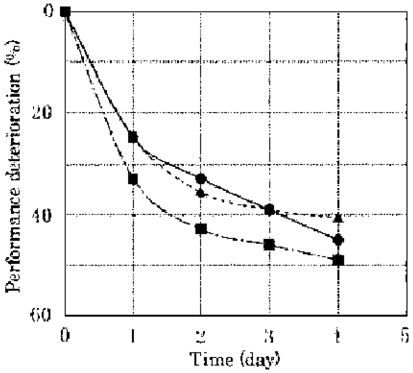
$$\text{Performance Deterioration} = \frac{\text{Remaining } SO_3H\,(\text{mole})}{\text{Initial } SO_3H\,(\text{mole})} \times 100$$

Improved heat-resistance is one of the strong demands from IERs users including potential ones in accordance with the expansion of IER applications. DIAION® RCP145H has been developed in compliance with such demands from catalyst-use, in particular, and it has not only good heat-resisting property but also high acidity as sufficient active catalyst at low temperatures: there is a report that higher selectivity is accomplished at lower temperatures than standard conditions.

SBAERs are poor in heat-resisting property as already explained. Figures X-1-11 and X-1-12 illustrate their decomposition mechanism and the correlation between degrees of crosslinkage and deterioration rates, respectively for references.



[Fig.X-1-11] Decomposition of SBAERs



[Fig.X-1-12] Decomposition of SBAER

Functional group: $-N(CH_3)_3$

Temp.: 120°C

Solvent: Water

▲: DVB 3 %

■: DVB 5 %

●: DVB 8 %

(5) Experimental method

The experiments with IERs as catalysts can be carried out after the following methods:

i) Batch method

Reactions are carried out by pouring IERs into reactant solutions under controlled temperature. Analyzing the reaction products in the reaction mother liquor from that the IERs are filtered out confirms the IERs' ability as catalyst. This is a convenient method to screen various kinds of IERs in the early investigation.

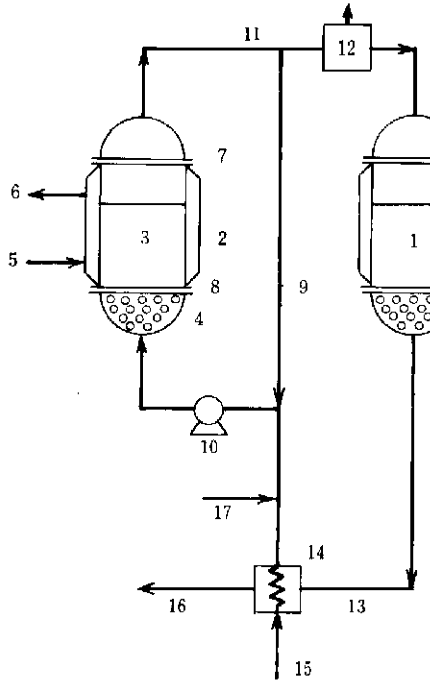
ii) Column method

Reactions are carried out at the controlled temperature in the columns filled with the objective IERs and the reactants are fed continuously. Not only the temperature but also the flow rate and the inner pressure should be controlled properly. This method is useful to investigate and to confirm the precise operation conditions and the scale-up factors about the selected IERs.

iii) Soxhlet extractor method

When reactants have low boiling points, Soxhlet extractors are used. The tested IERs are packed in a Soxhlet extractor and the reaction occurs under refluxing.

Fig.X-1-13 illustrates an example of model column reactors that is used to investigate hydrolysis reactions.



1. IERs
2. Jacket
3. IERs
4. Raschig ring
5. Inlet of Heating medium
6. Outlet of Heating medium
7. Strainer/Perforated plate
8. Strainer/Perforated plate
9. Closed circuit
10. Circulating pump
11. Pipe
12. Removal tower of Alcohol
13. Pipe
14. Heat exchanger
15. Water pipe
16. Pipe
17. Reactant feed

[Fig.X-1-13] Reactor tower model of reactions with IERs as catalysts; Hydrolysis

(6) Hydrolysis of Methyl acetate

The hydrolysis of methyl acetate is one of the representative reactions in which IERs have been applied traditionally. Methyl acetate is a byproduct in the polyvinylalcohol manufacturing and is hydrolyzed into acetic acid and methanol to be reused as starting materials to produce polyvinylalcohol. The relevant data are as follows:

$$CH_3COOCH_3 + H_2O \underset{k''}{\overset{k}{\rightleftarrows}} CH_3COOH + CH_3OH$$

$$a_0 - x \qquad b_0 - x \qquad x \qquad x$$

$a_0 : b_0 = 1 : 20$
Temp. = 30℃
x = molar conc. (mol/L)

irreversible first-order reaction rate constant: k_1

$$\frac{dx}{dt} = k_1(a_0 - x)$$

$$k_1 = \frac{1}{t}\ln\frac{a_0}{a_0 - x}$$

second-order reaction constant: k_2

$$\frac{dx}{dt} = k_2(a_0 - x)(b_0 - x) - k_{-2}x^2$$

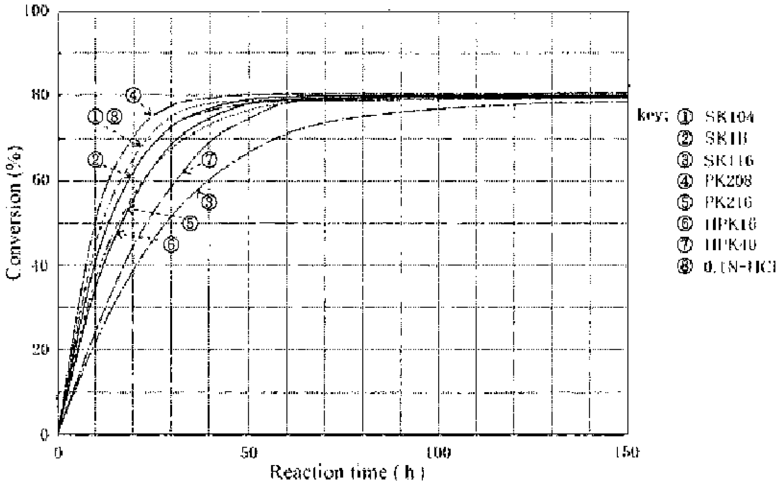
$$k_2 = \frac{1}{m} \bullet \frac{1}{t}\left[\ln\frac{(a_0 + b_0) - m - 2(1 - 4k)x}{(a_0 + b_0) + m - 2(1 - 4k)x} - \ln\frac{(a_0 + b_0) - m}{(a_0 + b_0) + m}\right]$$

$$m = \sqrt{(a_0 + b_0) - 4a_0 b_0 (1 - 4k)}$$

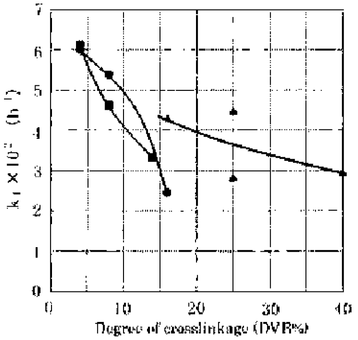
$$k = \frac{k_2}{k_{-2}}$$

SK104H and PK208H of low degree of crosslinkage are effective from the point of reaction rates, as illustrated in Fig.X-1-14. However, the IERs the degree of crosslinkage of which is over 8% are generally used, considering oxidation resistance.

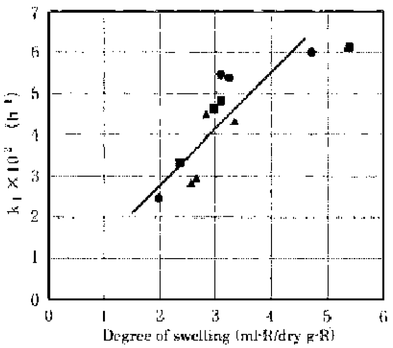
Fig.X-1-15 which demonstrates IERs of several degrees of crosslinkage and their observed first-order reaction rate constants, k_1 on acid, explains that highly porous-type resins are not always suitable for this reaction. Similarly, Fig.X-1-16 of k_1 and degrees of swelling shows the close correlation between them.



[Fig.X-1-14] Reaction rate and Conversion of Methyl acetate Hydrolysis
Conditions: Water/Ester: 20 (molar ratio) Catalyst conc.: 0.1N as H
Temp: 30 °C Stirring: 200 rpm
Particle size: 600 ~850 µm



[Fig.X-1-15] Degree of crosslinkage (DVB%) vs. in k_1 on acid of Methyl acetate Hydrolysis
Conditions: Water/Ester = 20 (molar ratio)
Temp. = 30 °C
Particle size = 600 ~850 µm

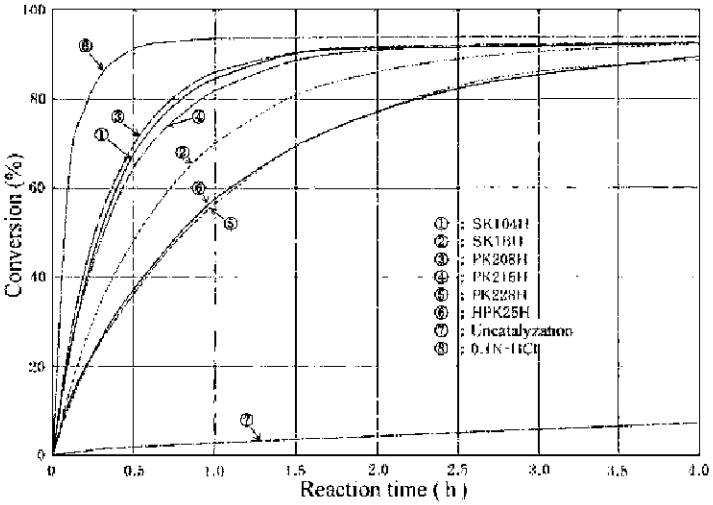


[Fig.X-1-16] Degree of swelling vs. in k1 on acid of Methyl acetate Hydrolysis
Conditions: Water/Ester = 20 (molar ratio)
Temp. = 30 °C
Particle size = 600 ~850 µm

●: Gel-type IER ■: Porous-type IER ▲: Highly porous-type IER

(7) Esterification

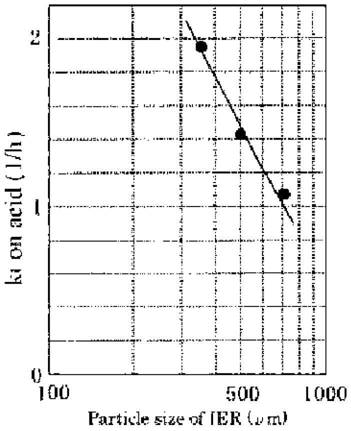
Methyl esterification of acetic acid is illustrated below as an example of esterification reactions: Fig.X-1-17 shows that IERs of low degrees of crosslinkage have high reaction rates. Fig.X-1-18 of particle sizes and also informs that k_1 depends on particle sizes. Still, standard size IERs, 500 ~600 µm in average, are usually used considering operativeness such as pressure drops.



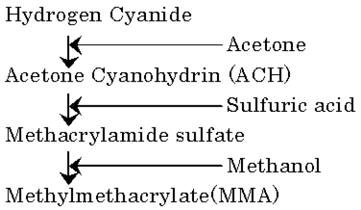
[Fig.X-1-17] Conversion vs. Reaction time of Esterification of Acetic acid
Conditions: Alcohol/ Acid: 5 (molar ratio) Catalyst conc.: 0.1N as H
Particle size: 425 ~600 µm Temp: 80 °C

(8) Synthesis of Methylmethacrylate

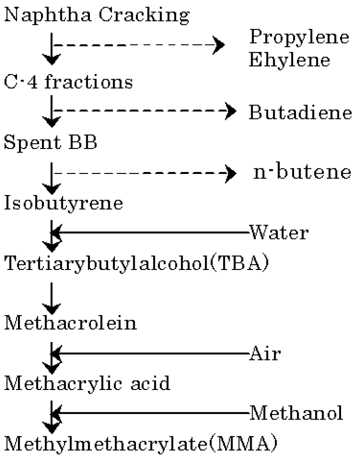
Methylmethacrylate has been manufactured traditionally by the ACH, acetone cyanohydrins, method illustrated in Fig.X-1-19. In recent years, however, because of the shortage of hydrogen cyanide as a starting material, two other methods are developed: one is by direct oxidation of isobutyrene or C-4 fractions, spent BB fraction, containing isobutyrene, and the other is by two-step reactions from isobutyrene through methacrylonitrile, MAN, and methacrylamide. In these processes, IERs are applied for the isolation of isobutyrene, the synthesis of tertiary butylalcohol (TBA) and the methyl esterification. Fig.X-1-21 demonstrates the correlation between the reaction conversions and times with several IER-grades. This figure shows that IER-grades of low degrees of crosslinkage have high catalyst-activity in the initial period of the reaction.



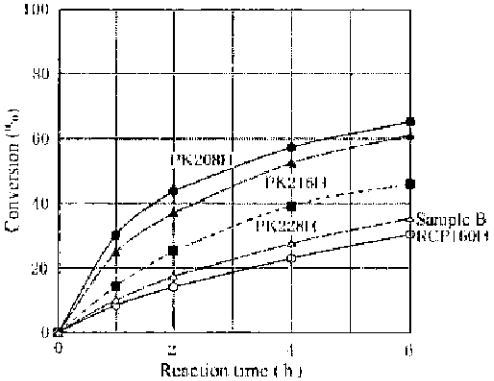
[Fig.X-1-18] k_1 vs. Particle size
IER : SK1B
Alcohol/Acid : 5 (molar ratio)
Catalyst conc. : 0.1N as H
Temperature : 80 °C
Stirring : 200 rpm



[Fig.X-1-19] Acetone Cyanohydrin method



[Fig.X-1-20] Direct oxidation of Isobutyrene



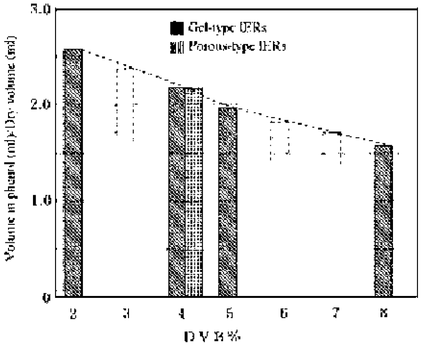
[Fig.X-1-21] Reaction time vs. Conversion of Methylmethacrylate synthesis
Temperature: 60 °C IER: Dry, 10 mL as wet
Methanol: 100 g Methacrylic acid: 27 g

(9) Bisphenol A

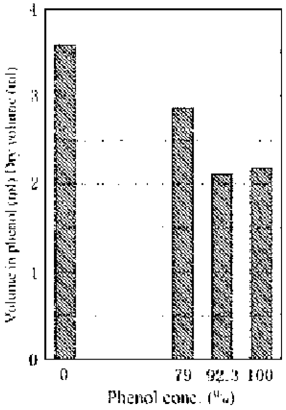
Polycarbonates highlighted as engineering plastics are manufactured from high purity bisphenol A. Such bisphenol A is produced with IERs as catalysts.

The degrees of swelling of IERs in phenol are illustrated in Figures X-1-22 and X-1-23, and Fig.X-1-24 demonstrates the reaction time and conversion curves of several kinds of IERs. The proper IERs for this reaction is the one some portion of the functional groups of that is modified to improve reaction selectivity. As such an example, the reaction time and conversion curves with H-form IER and with modified one by 2-aminoethanethiol are compared in Figures X-1-25 and X-1-26. As regards to degrees of crosslinkage, IERs of 4 ~6% are generally used. Gel-type IERs in H-form and porous-type ones in modified form are somewhat more effective in acetone conversion and reaction selectivity than other type IERs. When IERs are applied in H-form, their H-form conversion and water in them affect the reaction results, and thus IERs should be used in the state, e.g. H-conversion is over 98 ~99% and water is below 2%. IERs in modified form are thought to be in the same situation.

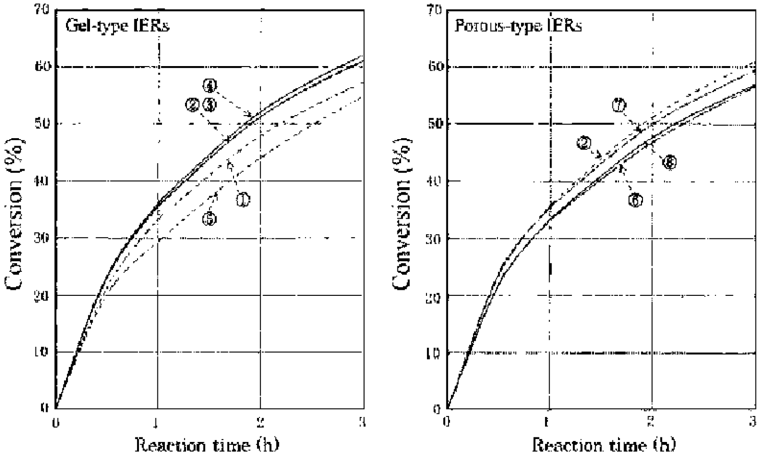
There are many patents and literatures concerning the applications of IERs as catalysts some parts of which are listed in TableX-1-5.



[Fig.X-1-22] Degree of Swelling of IERs in Phenol



[Fig.X-1-23] Degree of Swelling of SK104H in aq. Phenol

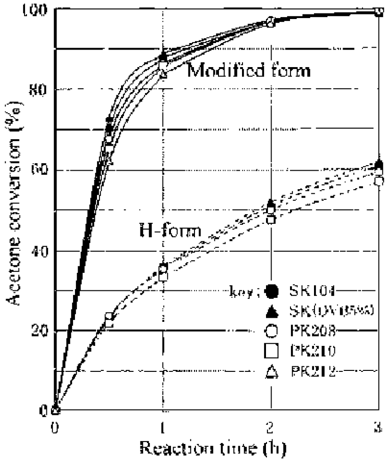


[Fig.X-1-24] Reaction time vs. Conversion of Bisphenol A synthesis

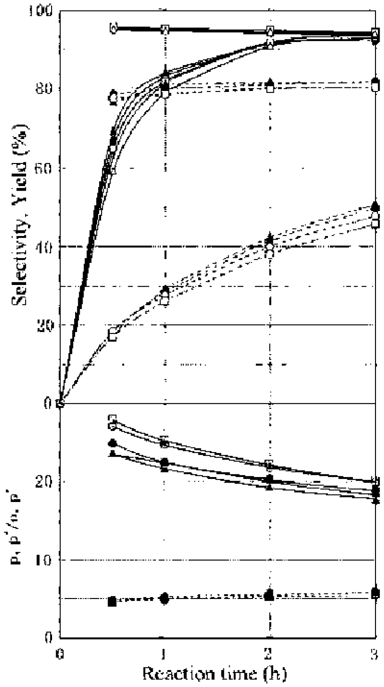
Phenol/Acetone	25 (molar ratio)
Reaction Liquor/IER, H-from	2.7 / 1 (volume ratio)
Temperature	60 °C

IER is pre-swelled in phenol at 80°C, 5h after pre-expanding and regeneration of 1000g/l-R

① Gel-type , Degree of crosslinkage 3 %
② SK104H
③ Gel-type , Degree of crosslinkage 5 %
④ Gel-type , Degree of crosslinkage 6 %
⑤ SK1BH
⑥ Porous-type , Degree of crosslinkage 3 %
⑦ PK208H
⑧ Porous-type , Degree of crosslinkage 5 %

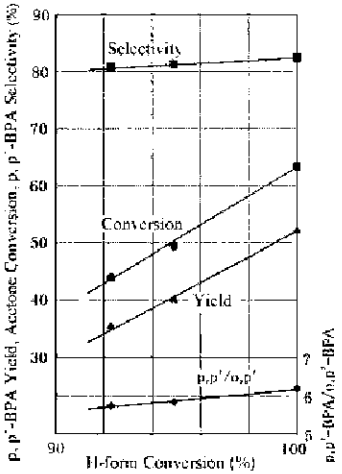


[Fig.X-1-25] Effect of Functional groups to Conversion
Modified IERs: 10% of functional groups are modified by
1-aminoethanethiol hydrochloride



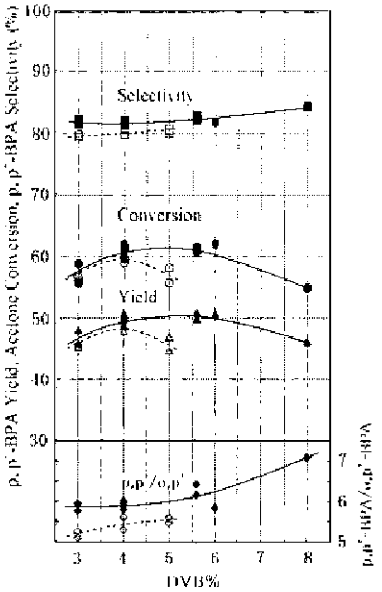
[Fig.X-1-26] Effect of Functional groups to Yield and Conversion

- ● SK104
- ▲ SK(DVB6%)
- ○ PK208
- □ PK (DVB5%)
- △ PK212
- — Modified
- --- H-form



[Fig.X-1-27] Effects of H-form Conversion of SK104H in Bisphenol A synthesis

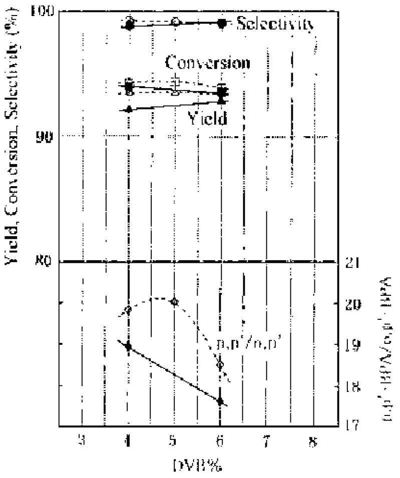
- ■ p, p'-BPA Selectivity (%)
- ● Acetone Conversion (%)
- ▲ p, p'-BPA Yield (%)
- ◆ p ,p'-BPA /o, p'-BPA (molar ratio)



[Fig.X-1-28] Effects of Degree of Crosslinkage to Yield, Conversion and Selectivity: H-form IERs

●■▲ Gel-type IERs

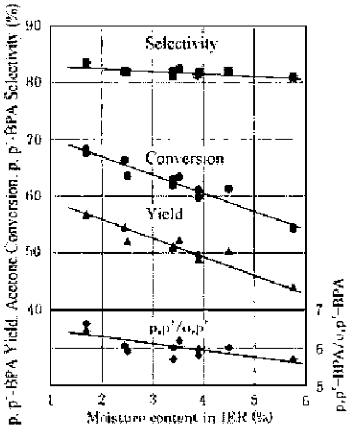
○□△ Porous-type IERs



[Fig.X-1-29] Effects of Degree of Crosslinkage to Yield, Conversion and Selectivity: Modified IERs

●■▲ Gel-type IERs

○□△ Porous-type IERs



[Fig.X-1-30] Effect of Moisture content in SK104H in Bisphenol A Synthesis

■ p,p'-BPA Selectivity (%)

● Acetone Conversion (%)

▲ p,p'-BPA Yield(%)

◆ p,p'-BPA /o,p'-BPA (molar ratio)

[TableX-1-5] Literatures about IERs as catalysts

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