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Studies of Polystyrene-based Ion Exchange Fiber. II. A Novel Fiber-form Catalyst for Sucrose Inversion and Methyl Acetate Hydrolysis[†]

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To obtain a novel acid-base catalyst of high activity and easy treatment, we have prepared polystyrene-based fibrous ion exchange catalysts which have large surface areas per unit of weight and which can be utilized in various forms. They are excellent in chemical stability and mechanical strength due to their composite structures, reinforced with polypropyrene. The reactions of sucrose inversion and methyl acetate hydrolysis were carried out by using these cation exchange fibers and ordinary cation exchange resins. The fiber has about sixteen times as high a catalytic activity per equivalent acid as the resin in the case of sucrose inversion. The intrinsic rate constant in the fiber phase is evaluated to be 2.4 times larger than that in the resin phase in terms of the solid-catalysis theory considering the catalytic effectiveness factor and the absorption coefficient. On the other hand, the catalytic activity per equivalent acid of the fiber is almost equal to that of the resin in the case of methyl acetate hydrolysis. It is suggested that this different behavior is attributable to the different molecular sizes of the reactants.

Polystyrene-based ion exchange resins have been intensively studied as solid acid-base catalysts in a number of organic reactions.[2] The use of ion exchange resins, however, has the disadvantage that their catalytic activities per equivalent acid or base are lower than those of free acids or bases in the case of a reaction controlled by intraparticle diffusion. Although catalytic activity is enhanced by using a fine or crushed resin, catalytic treatment becomes difficult.

In order to enhance the catalytic activity and to make catalytic treatment easier, we have undertaken an investigation of fibrous acid-base catalysts, which have large surface areas per unit of weight and which can be used in various forms. Polystyrene-based fibrous ion exchange catalysts have been prepared and used in the well-known reactions of sucrose inversion and methyl acetate hydrolysis.[3] These results will be discussed in terms of the solid-catalysis theory in this paper.

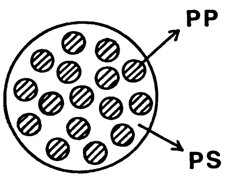

Fig. 1. Schematic cross section of composite fiber. PSt: polystyrene, *sea* ingredient; PP: polypropylene, *island* ingredient.

Fig. 2. Process of preparing the polystyrene-based ion exchange fiber (IONEX).[1]

Experimental

Polystyrene (PSt; average molecular weight: 23×10^4) as the predominant *sea* ingredient and polypropylene (PP; average molecular weight: 20×10^4) as the *island* ingredient were spun into composite filaments having an *islands-in-a-sea* type sectional structure, as is shown in Fig. 1, in the conventional manner. Polystyrene-based ion exchange fibers, named IONEX, were prepared according to the process shown in Fig. 2 after spinning.[1] The crosslinking was performed by treating the fiber (10 g) with 100 ml of a solution consisting of 5 wt% paraformaldehyde, 25 wt% acetic acid, and 70 wt% concd. sulfuric acid at 80 °C for 2 h or at 90 °C for 4 h.[4] Fibrous acid or base catalysts were obtained by treating these fibers with an acid or a base in the usual manner.

These fibrous cation exchange catalysts were packed into a jacketed glass fixed-bed reactor with an inside diameter of 2 cm. The reactions of sucrose inversion and methyl acetate hydrolysis were carried out by pumping a 50 wt% sucrose aqueous solution at 60 °C and a 3.2 M (1 M=1 mol dm^{-3}) methyl acetate aqueous solution at 30 °C respectively through the reactor. For the purposes of comparison, the reactions were also carried out by using commercially available cation exchange resins (Amberlite IR-120B and IR-200) with radii of *ca.* 250 μm. The reaction ratio of sucrose was measured according to the usual polarimetric technique.[5] The acetic acid concentration was determined by the titration method.

Results and Discussion

Fibrous Acid-base Catalyst. The characteristic data of the filamentary IONEX are summarized in Table 1. Acid-base catalysts in various forms, such as cut fiber, knitted fabric, woven fabric, braid, felt, nonwoven fabric, and paper, can be obtained by processing the filaments before chemical reactions, as the filaments reinforced with polypropylene have high mechanical strengths. Figure 3 shows fibrous cation

TABLE 1. CHARACTERISTIC DATA OF FILAMENTARY IONEX

Ionic group[a)]	Diameter	Strength	Capacity[b)]	Water content[c)]
	μm	g d^{-1}	mequiv g^{-1}	
—	24	3.0	—	—
-SO$_3^-$	30	1.3	2.6	1.6
-N$^+$(CH$_3$)$_3$	32	1.4	2.4	1.9

a) Original filaments: *Sea* (PSt//PP)/*Islands* (PP)=(40//10)/50. b) Capacity of strong-acid (base) groups. c) $(W-W_0)/W_0$. W: wet weight, W_0: dry weight.

[†] A preliminary report of this work was presented in *Shokubai*, **25**, 115 (1983).

Table 2. Results of sucrose inversion by various acid catalysts

No.	Acid catalyst	Capacity	Water content	Bed volume$^{a)}$	Packed weight	Rate constant$^{b)}$ $k \times 10^3$
		mequiv g^{-1}		ml	g	ml s^{-1} mequiv^{-1}
1	Filamentary IONEX	2.5	2.0	37.5	4.0	12.4
2	Filamentary IONEX	2.5	1.6	25	2.9	12.7
3	Knitted IONEX	2.5	1.6	25	5.3	8.9
4	Amberlite IR-120B	5.0	0.9	25	10	0.80
5	Amberlite IR-200	4.8	1.0	25	10	0.88

a) Diameter: 2 cm. b) 60 °C, 50 wt% sucrose aqueous solution.

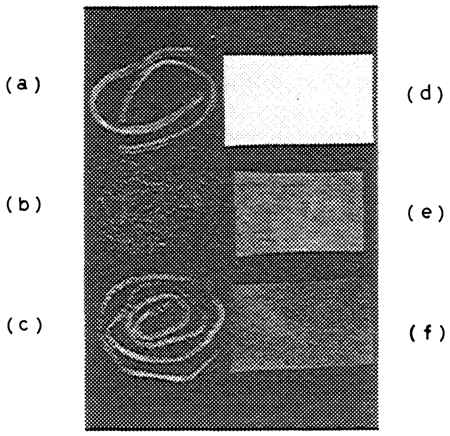

Fig. 3. Fibrous cation exchange catalyst in various forms of knitted cord (a), filament (b), braid (c), paper (d), knitted fabric (e), and needle punched felt (f).

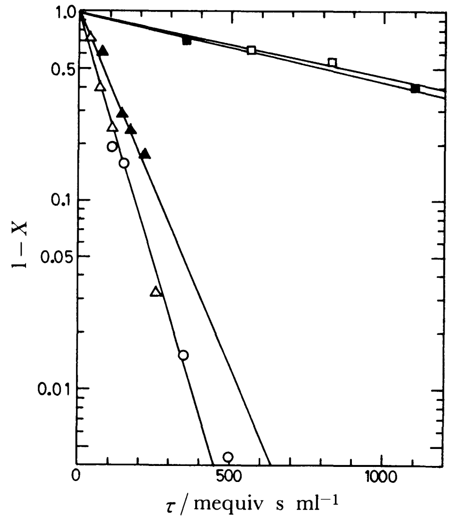

Fig. 4. Plots of $1-X$ *vs.* τ in sucrose inversion (Eq. 1). Reaction temperature, 60 °C; concentration of sucrose solution, 50 wt%.
○: Filamentary IONEX (water content 2.0), △: filamentary IONEX (water content 1.6), ▲: knitted IONEX (water content 1.6), □: Amberlite IR-120B, ■: Amberlite IR-200.

exchange catalysts in various forms. The ion exchange capacities per unit of weight of IONEX are lower than those of ordinary ion exchange resins by the amount of polypropyrene used for reinforcement.

Sucrose Inversion. The results of sucrose inversion by various acid catalysts are shown in Fig. 4 and Table 2. On the assumption of first-order kinetics, the apparent rate constant, k, was determined from the following equation:

$$\ln(1-X) = -k\tau, \tag{1}$$

where X is a reaction ratio of sucrose and where τ is a contact time.

The effect of the packing density of the fibers was also examined. In the density range above 0.1 g ml^{-1} the rate constant is close to the value of 13.4×10^{-3} ml s^{-1} mequiv^{-1} determined by a batch method. However, below 0.1 g ml^{-1} it decreases slightly as the density is lowered, probably because of the effect of an irregular flow. It was found that the height of the fixed-bed and the crosslinking degree of the fiber do not affect the rate constant. The catalytic activity of the knitted IONEX is 30% lower than that of the filamentary IONEX. This result may be interpreted by assuming that the effective surface area per unit of weight decreases or an irregular flow takes place because of the knitted structure.

The apparent rate constant of the filamentary IONEX is about sixteen times as large as that of the gel-type resin, IR-120B. According to the solid-catalysis theory, the apparent rate constant, k, can be described by the following equation:[6,7]

$$k = \lambda k_0 \eta, \tag{2}$$

where λ, k_0, and η are an absorption coefficient, an intrinsic rate constant, and a catalytic effectiveness factor respectively. Here, the catalytic effectiveness factors in the two cases of spherical and fibrous catalysts with a given radius, R, are given by:[8]

$$\eta(\text{sphere}) = \frac{3(mR\coth mR - 1)}{(mR)^2} \tag{3}$$

and

$$\eta(\text{fiber}) = \frac{2I_1(mR)}{I_0(mR)} \tag{4}$$

respectively, where I_0 and I_1 are modified Bessel functions of zero and first-order and where $m = \sqrt{k_0/D}$, in which D is an effective diffusion coefficient of a reactant in a catalyst. The relation between m and η in the two cases of the spherical catalyst with a radius of 250 μm and the fibrous catalyst with a radius of 15 μm is shown in Fig. 5.

The value of η for IR-120B is larger than 0.25, judging from the results studied by Gilliland *et al.*,[7] so that the value of η for the fiber can be roughly evaluated

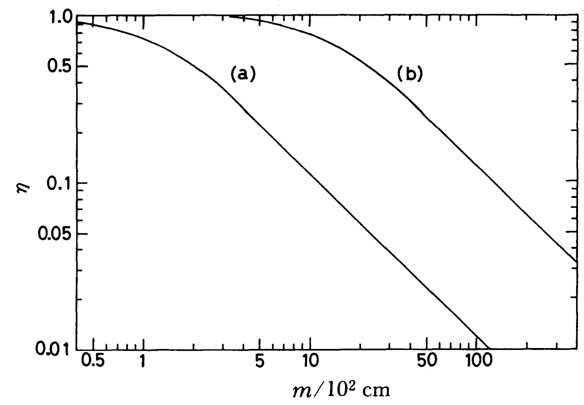

Fig. 5. Catalytic effectiveness factor η as a function of m (Eqs. 3 and 4).
(a) Spherical catalyst (R= 250 μm), and (b) fibrous catalyst (R=15 μm).

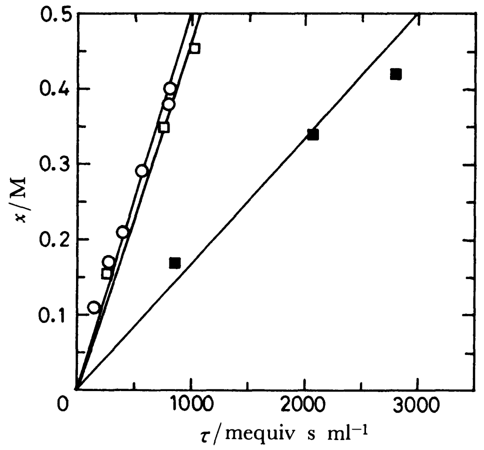

Fig. 6. Plots of x *vs.* τ in methyl acetate hydrolysis (Eq. 5).
Reaction temperature, 30°C; concentration of methyl acetate solution, 3.2 M.
○: Filamentary IONEX (water content 2.0), □: Amberlite IR-120B, ■: Amberlite IR-200.

to be almost equal to 1 at the corresponding m-value from Fig. 5. The sucrose-absorption coefficients for IR-120B and the fiber in a Na form were found to be 0.30±0.05 and 0.50±0.1 in a 50 wt% sucrose aqueous solution. The former value is much larger than that in a 20 wt/vol% sucrose aqueous solution determined by Gilliland *et al.*7) It is, however, considered to be an adequate value, because the absorption coefficient generally increases as the concentration of sucrose in a solution increases. Probably the absorption coefficient of the fiber is larger than that of the resin because of the difference in water contents; that is, the fiber has a higher water content than the resin.6)

In considering the results described above, the experimental data show that the intrinsic rate constant in the fiber phase is 2.4 times larger than that in the resin phase. It has been reported by Gilliland *et al.* that the intrinsic rate constants in the resin phase are only 60% as large as those determined in 3 M acid solutions.7) The reason for the reduced effectiveness of the resin as a catalyst has been attributed to an irregular structure of the crosslinked resin and to steric hindrance due to a large reactant of the sucrose molecule. The fact that the fiber has a higher intrinsic rate constant than the resin may be explained by assuming that the fiber has such a crosslinked structure that the steric hindrance is relieved. That is, the fiber based on polystrene essentially has a less restricted one-dimensional structure although its chains are crosslinked by methylene bonds, while the resin based on a styrene–divinylbenzene polymer has a more restricted three-dimensional structure. The difference in the intrinsic rate constants may be enhanced by the high sucrose concentration of 50 wt%.

On the other hand, the catalytic effectiveness factor for IR-200 of the macroreticular type can be estimated to be 1 from its large surface area of 50 m^2 g^{-1}. Its absorption coefficient for sucrose was measured as 0.40±0.05. Taking these facts into account, the intrinsic rate constant in the IR-200 phase is found to be only 20% as large as that in the IR-120B phase. This may be attributable to the large effect of the steric hindrance, which prevents a close approach of a sucrose molecule to an active site for inversion, because the macroreticular-type resin is three-dimensionally and tightly crosslinked.7,9)

Methyl Acetate Hydrolysis. The reaction of methyl acetate hydrolysis was carried out by using the Nos. 1, 4, and 5 beds shown in Table 2. The acetic acid concentrations in effluent solutions as a function of the contact times are shown in Fig. 6. As this reaction is first-order, the apparent rate constant can be evaluated from the following equation:

$$\ln a/(a-x) = k\tau, \tag{5}$$

where x is an acetic acid concentration and a is its concentration in equilibrium. It is possible to evaluate the apparent rate constants directly from Fig. 6, since k is equal to $x/a\tau$ when x is sufficiently small.

No large difference in the apparent rate constants was observed between the fiber and IR-120B. This fact indicates that their catalytic effectiveness factors are both close to 1 because of the probable rapid diffusion of methyl acetate molecules in the catalysts, and that both the absorption coefficient and the intrinsic rate constant of the fiber are almost equal to those of the resin.6,10) On the other hand, the apparent rate constant for IR-200 is only one third as large as that for IR-120B. This result can be interpreted by assuming that the former has a small absorption coefficient and also has a small intrinsic rate constant because of the steric hindrance in comparison with the latter, although their catalytic effectiveness factors are both close to 1.11)

The fibrous catalyst is expected to be applicable to new reactors such as the reaction distiller of methyl acetate hydrolysis, since it can be used in various forms.12,13)

Conclusion

1. Polystyrene-based fibrous ion exchange catalysts which are excellent in chemical stability and mechanical strength have been prepared. These fibrous acid-base catalysts have a large surface areas per unit of

weight and can be used in various forms.

2. These ion exchange fibers have not only much higher catalytic activities than ordinary ion exchange resins when the reactant is a large molecule such as sucrose, but also the advantage of easier catalytic treatment than a fine or crushed resin.

3. When the reactant is a small molecule such as methyl acetate, these ion exchange fiber show as high catalytic activities as ordinary ion exchange resins.

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