JOURNAL OF CATALYSIS **149**, 243–245 (1994)

NOTE

Sulfonic Acid Catalysts Prepared by Radiation-Induced Graft Polymerization

Ion-exchange resin (IER) beads containing a sulfonic acid (SO_3H) group are used as catalysts for hydrolysis of methyl acetate (1) and synthesis of methyl tertiary butyl ether (MTBE) (2). These reactions can be accelerated by combination with distillation of the product, which is known as reactive distillation. At present, a packing material assembled by elaborately entrapping the ion-exchange beads is loaded into a reactive distillation column (3); however, more efficient reactive distillation demands a simple packing material suitable for vapor–liquid contact in the column.

We have so far suggested a simple introduction of the SO_3H group onto various forms of a trunk polymer, such as a hollow fiber, tube, nonwoven fabric and film, by applying radiation-induced graft polymerization (RIGP) (4). Moreover, the SO_3H group anchored to the grafted polymer chains showed a higher hydrolytic activity for sucrose, compared to the SO_3H group introduced into the polystyrene chain cross-linked with divinylbenzene (DVB), because of the absence of steric hindrance (5).

In this study, we prepared two variations of graft-type acid catalyst with different adjacent groups by RIGP, and compared the hydrolytic activity of the resultant acid catalysts for methyl acetate with that of commercially available SO_3H-type ion-exchange beads with different degrees of cross-linking.

The sulfonic acid (SO_3H) group was introduced onto a polyethylene (PE) microporous hollow fiber by two schemes, as illustrated in Fig. 1. Scheme (A) shows cografting of originally SO_3H-group-containing vinyl monomer (sodium *p*-styrenesulfonate, $CH_2{=}CHC_6H_4SO_3Na$, SSS) with 2-hydroxyethyl methacrylate ($CH_2{=}CCH_3COOCH_2CH_2OH$, HEMA) onto the irradiated PE matrix (6), and scheme (B) shows grafting of epoxide-group-containing vinyl monomer (glycidyl methacrylate, $CH_2{=}CCH_3COOCH_2CHOCH_2$, GMA) onto the PE matrix with subsequent ring-opening of the epoxide with sodium sulfite (Na_2SO_3, SS) and water addition to the remaining epoxide (7). These two resultant acid catalysts will be referred to as SSS/HEMA-T and GMA-SS-T fibers, respectively, where T denotes tubularity. The thickness of the SSS/HEMA-T and GMA-SS-T fibers was about 1.2 mm in a wet state. The polymer chains grafted onto the PE matrix contain two and three moieties, respectively: SO_3H and alcoholic hydroxyl (monool) groups for the SSS/HEMA-T fiber, and SO_3H, monool, and adjacent alcoholic hydroxyl (diol) groups for the GMA-SS-T fiber. The total density of these moieties was calculated from the weight gain after chemical modifications; the SO_3H group density was determined by measuring the salt-splitting capacity. Here, we define a mole fraction of the SO_3H group in the grafted polymer chain as

$$\text{mole fraction} = [SO_3H]/([SO_3H] + [\text{monool}]) \quad \text{for the SSS/HEMA-T fiber,}$$

$$\text{mole fraction} = [SO_3H]/([SO_3H] + [\text{monool}] + 2[\text{diol}]) \quad \text{for the GMA-SS-T fiber,}$$

where $[SO_3H]$, [monool], and [diol] denote the number of moles of the SO_3H, monool, and diol groups, respectively.

The mole fraction of the SO_3H group of the SSS/HEMA-T fiber ranged from 0.20 to 0.59 upon cografting of SSS with HEMA. The GMA-SS-T fiber had a mole fraction ranging from 0.07 to 0.35 upon varying the conversion of the epoxide group into the SO_3H group with different degrees of GMA grafting.

The hydrolytic activity for methyl acetate of the SSS/HEMA-T and GMA-SS-T fibers was determined in a batch mode. Experimental apparatus and procedures are detailed in our previous paper (5). Briefly, a prescribed amount of about 5-mm-long cut hollow fibers was immersed in 100 g of 3 mol/kg methyl acetate aqueous solution, in which the molar ratio of the SO_3H group to the initial methyl acetate was set to 0.01. The reaction temperature ranged from 313 to 328 K. Kinetic data in a batch mode, i.e., the decrease in concentration of methyl acetate in a finite volume as a function of reaction time, could be analyzed to obtain an apparent reaction rate constant, k_a. For comparison, the following SO_3H-group-containing beads with different degrees of cross-linking, from Rohm and Haas Co., were used for determination of the hydrolytic activity of methyl acetate: Amberlite IR-120B

0021-9517/94 $6.00

(DVB 8%), Amberlite IR-124 (DVB 12%), and Amberlyst 15 (DVB 20%). Figures 2A and 2B show the apparent reaction rate constant as a function of the SO_3H group mole fraction of the SSS/HEMA-T and GMA/SS-T fibers, respectively. The difference in the hydrolytic activity between the SSS/HEMA-T and GMA-SS-T fibers is ascribed to the acidity: the benzene ring attracts electrons more strongly than methylene. In this study, k_a was constant irrespective of the density of adjacent groups such as monool and diol groups.

The Arrhenius plot, i.e., logarithm of k_a vs reciprocal of the reaction temperature, is shown in Fig. 3. The activation energy of 73 kJ/mol calculated from this figure was almost consistent with the value of 72 kJ/mol (8) determined in a homogeneous system, i.e., sulfuric acid. Consistency of the activation energy of the hydrolysis of methyl acetate among graft-type acid catalysts and cross-linked acid catalysts shows that the overall reaction is governed by the intrinsic catalytic reaction, not by the diffusion of methyl acetate into the hollow fibers and beads. Also, the pulverized fiber was found to exhibit the same result. Ion-exchange beads exhibited a lower activity with an increasing degree of cross-linking while maintaining the same activation energy. This is because the density of the SO_3H group which was accessed by methyl acetate was reduced by cross-linking of the polystyrene chains.

In conclusion, sulfonic acid catalysts prepared by radiation-induced graft polymerization of sodium *p*-styrenesulfonate with subsequent conversion to the H form had almost the same hydrolytic activity for methyl acetate as the SO_3H-type bead with the lowest degree of cross-linking. A new packing material for reactive distillation

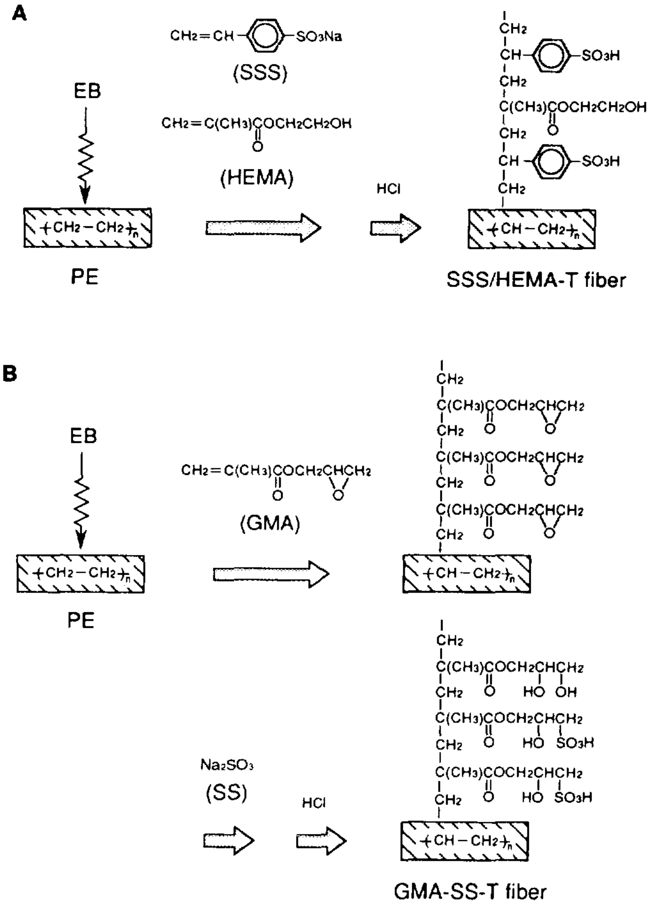

FIG. 1. Two variations of the introduction of SO_3H group into polyethylene microporous hollow fiber: (A) SSS/HEMA-T fiber and (B) GMA/SS-T fiber.

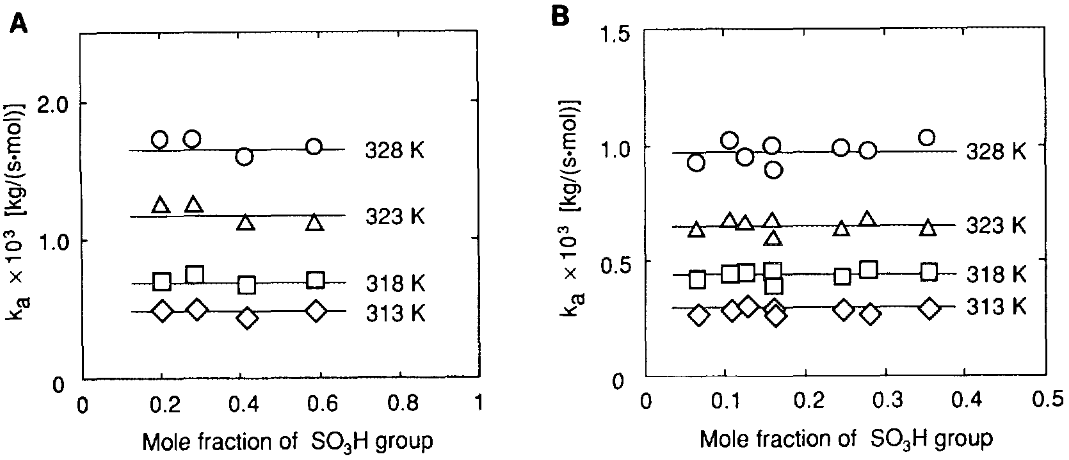

FIG. 2. Apparent reaction rate constant vs mole fraction of the SO_3H group: (A) SSS/HEMA-T fiber and (B) GMA/SS-T fiber.

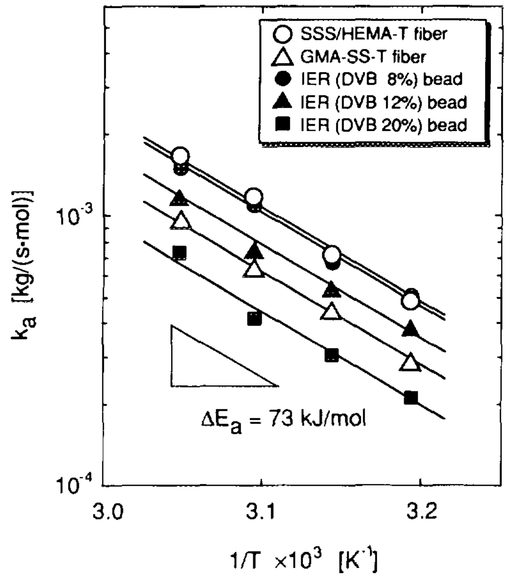

FIG. 3. Dependence of reaction rate constant on reaction temperature.

can be designed because the RIGP is applicable to various physical shapes of the trunk polymer.

ACKNOWLEDGMENTS

Helpful discussions with Mr. Makoto Chiwa of the Functional Material Division of Organo Co., Ltd., Japan, are gratefully acknowledged. We also wish to thank Mr. Yoshizumi Inai of the Industrial Membrane Division of Asahi Chemical Industry, Co., Ltd., Japan, for his help in providing the starting hollow fiber.

REFERENCES

1. Fuchigami, Y., *J. Chem. Eng. Jpn.* **23,** 354 (1990).
2. Dow Chemical Co., *Chem. Eng.* **Sept.,** 63 (1992).
3. Lander, E. P., Hubbart, J. N., and Smith, L. A., Jr., *Chem. Eng.* **Apr.,** 36 (1983).
4. Sugiyama, S., Tsuneda, S., Saito, K., Furusaki, S., Sugo, T., and Makuuchi, K., *React. Polym.* **21,** 187 (1993).
5. Mizota, T., Tsuneda, S., Saito, K., and Sugo, T., *Ind. Eng. Chem. Res.*, in press.
6. Tsuneda, S., Saito, K., Furusaki, S., Sugo, T., and Makuuchi, K., *Ind. Eng. Chem. Res.* **32,** 1464 (1993).
7. Tsuneda, S., Shinano, H., Saito, K., Furusaki, S., and Sugo, T., *Biotechnol. Prog.* **10,** 76 (1994).
8. Herbert, S. H., and Arthur, M. R., Jr., *J. Am. Chem. Soc.* **63,** 1993 (1941).

Tomotoshi Mizota*
Satoshi Tsuneda*
Kyoichi Saito*,[1]
Takanobu Sugo†

**Department of Chemical Engineering*
Faculty of Engineering
University of Tokyo
Hongo, Tokyo 113
Japan

†Takasaki Radiation Chemistry Research Establishment
Japan Atomic Energy Research Institute
Takasaki, Gunma 370-12
Japan

Received January 13, 1994; revised May 16, 1994

---

[1] To whom correspondence should be addressed.