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種別(和文)	要約
Type(English)	Outline

Summary of Doctor Thesis

Synthesis of ester polymer by solid acid catalyst
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1. INTRODUCTION

Esterification is one of the most important reactions in chemical industry for the production of plastics and polymers.^{1),2)} Homogeneous acids, such as H₂SO₄ and p-toluenesulfonic acid, were conventionally used in industrial esterification processes; however, the use of these catalysts requires energy-inefficient processes for separation, recycling, and treatment of the spent acid. This has stimulated the replacement of homogeneous catalysts with stable, easily separable, and highly active heterogeneous catalysts that can be isolated from reaction mixture by simple decantation or filtration and be used repeatedly for the subsequent reactions. In this study, I focused on unique catalysis of MoO₃/ZrO₂ and sulfonated carbon solid acid catalyst (CSA)^{3),4)} and applied these strong Brønsted acids to the polyesterification of adipic acid with 1,4-butanediol and acryloylation of hyperbranched polyether-polyol with acrylic acid, respectively.

2. Polyester polyol synthesis using MoO₃/ZrO₂ catalyst

2.1 EXPERIMENTS

MoO₃/ZrO₂ (Mo/Zr = 0.1) was prepared by impregnation method. An aqueous solution of ammonium molybdate was added to Zr(OH)₄. After evaporation of water, the Mo-impregnated Zr(OH)₄ was dried at 373 K overnight and then calcined at 1073 K for 3 h in air.

Catalytic performance was tested by the formation of polyester polyol. Polyester precursor was prepared from 1,4-butanediol and adipic acid. A mixture of polyester precursor (50 g) and acid catalyst (0.05 g) was heated at 448 K for 8 h under an ambient pressure. The solutions were taken at intervals, and AN and OH value of the product were estimated by acid-base titration. For comparison, tetraisopropyl titanate, niobic acid (Nb₂O₅·nH₂O, Companhia Brasileira de Metalurgia e Mineração), H-beta (Zeolite, HSZ-940HOA, Tosoh), H-mordenite (Zeolite, HSZ-640HOA, Tosoh), and sulfated zirconia (SO₄²⁻/ZrO₂, supplied from Daiichi kigenso kagaku kogyo Co.,Ltd.) were also examined under the same reaction conditions. The amount of residual catalyst in the resulting final product was estimated with inductively coupled plasma-atomic emission spectrometry (ICP-AES).

2.2 RESULTS and DISCUSSION

MoO₃/ZrO₂ was composed of tetragonal and monoclinic ZrO₂, and hexagonal ZrMo₂O₈. Acid site density and the acid strength (H₀) of the MoO₃/ZrO₂ were estimated by NH₃ temperature-programming desorption analysis to be 0.16 mmol g⁻¹ and ca. -13, respectively. Figure 1 shows time courses for polyester polyol formation over various acid catalysts. MoO₃/ZrO₂ exhibits high catalytic performance for the polyesterification of 1,4-butanediol and adipic acid, whereas other solid acids, such as Nb₂O₅·nH₂O, zeolites, and SO₄²⁻/ZrO₂, are not effective for the reaction. After reaction, the MoO₃/ZrO₂ catalyst was easily recovered by simple filtration and used repeatedly without significant loss of original activity for subsequent reactions. In addition to stability and high activity, the amount of residual Mo and Zr species within the resulting polymer was below 3 ppm. By contrast, large amounts of metal species are incorporated into the resulting polymer when homogeneous catalyst including tetraisopropyl titanate is used as a catalyst. Weak interaction of MoO₃/ZrO₂ surface with reactant molecules. Appropriate acid strength on MoO₃/ZrO₂ results in high catalysis for polyesterification of adipic acid with 1,4-butanediol.

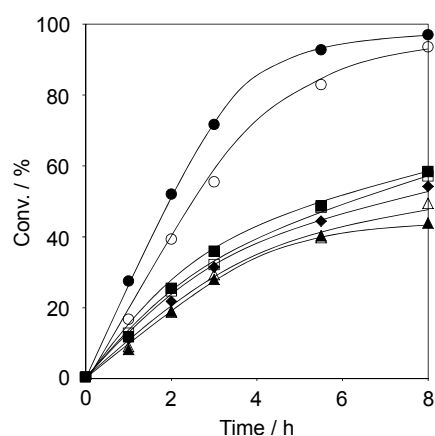


Figure 1. Time course for polyesterification of adipic acid with 1,4-butanediol over various acid catalysts at 448 K. ●; MoO₃/ZrO₂, ○; Isopropyl titanate, ■; SO₄²⁻/ZrO₂, □; Nb₂O₅·nH₂O, ▲; β-zeolite, △; mordenite, ◆; no catalyst.

3. Acryloylation reaction of hyperbranched polyetherpolyol with acrylic acid by CSA

3.1 EXPERIMENTS

CSA was prepared by using partial carbonization of a microcrystalline cellulose powder (Avicel, Merck) and sulfonation of the resulting carbon precursor in a fuming H_2SO_4 solution. The microcrystalline cellulose was heated to 673 K for 5 h under flowing N_2 to produce incompletely carbonized materials as precursors. The carbon precursors were then warmed in a fuming H_2SO_4 solution (15 wt%) at 353 K for 10 h. The resulting materials were washed repeatedly with hot distilled water until the pH of the filtrate became neutral, after which the filtrate was dried at 333 K for 12 h.

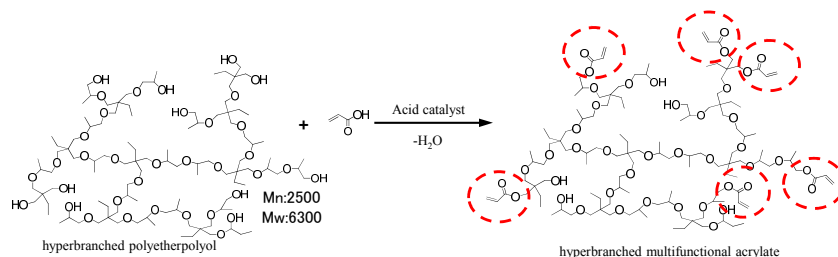


Figure 2. Reaction scheme for hyperbranched multifunctional acrylate

Hyperbranched multifunctional acrylate was synthesized by esterification of hyperbranched polyetherpolyol with acrylic acid (Figure 2). CSA and reference catalysts (DIAION: polystyrene-based strong acid ion-exchange resin supplied from Mitsubishi Chemical Corporation and p-toluenesulfonic acid monohydrate) were used as acid catalysts in this study. Hyperbranched polyether polyol (60.0 g), acrylic acid (16.0 g), p-methoxyphenol (0.15 g), cyclohexane (42.0 g), toluene (18.0 g), and catalyst (0.6 ~ 6.0 g) were added to the 300 ml four-necked flask equipped with a Dean-Stark apparatus, air inlet tube, stirring apparatus, and a thermometer. The reaction was carried out with azeotropic removal of condensed water and solvent at 358 K with bubbling dry air. OH value in the isolated product was estimated by acid-base titration. Conversion (%) was calculated based on hydroxyl value of polyether-polyol before and after the reaction. Molecular weight of products was estimated by GPC measurement.

3.2 RESULTS and DISCUSSION

CSA consisted of flexible polycyclic aromatic carbon nanosheets with high densities of SO_3H , COOH and phenolic OH groups in a three-dimensional network.⁴⁾ Figure 3 shows time courses for polyether-polyol conversion over CSA and reference catalysts. CSA and p-toluenesulfonic acid show high catalytic activity for the reaction. Although DIAION (SO_3H group: 4.2 mmol g^{-1}) has large amounts of SO_3H group than CSA (SO_3H group: 1.3 mmol g^{-1}), the reaction does not proceed on DIAION at all. This difference is attributed to adsorption property of bulk alcohol, such as polyether-polyol. Although CSA can incorporate large amounts of polyether-polyol into the bulk, DIAION cannot adsorb such hydrophobic alcohol. Since DIAION and CSA have small surface area ($< 5 \text{ m}^2 \text{ g}^{-1}$), most of SO_3H are located inside the particles. Thus, smooth incorporation property of CSA enables the access of bulk polyether-polyol to SO_3H groups, which results in high catalytic performance. In the case of DIAION, the reaction proceeds only on SO_3H groups on outer surface with small surface area. Because of small amounts of effective SO_3H groups, DIAION shows no or poor catalysis.

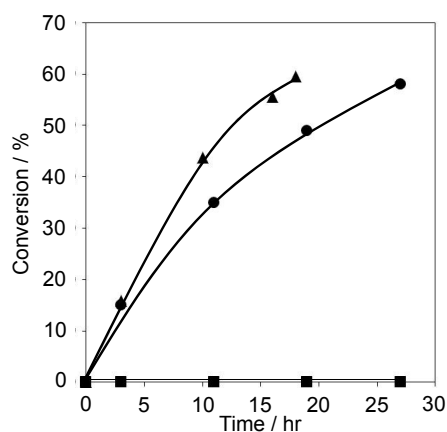


Figure 3. Time course for acryloylation of hyperbranched polyetherpolyol with acrylic acid over various acid catalysts at 358 K. ●; CSA, ■; Ion exchange resin, ▲; p-toluenesulfonic acid

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