論文 / 著書情報
Article / Book Information

題目(和文)	固体酸触媒によるエステルポリマーの合成
Title(English)	Synthesis of ester polymer by solid acid catalyst
著者(和文)	沖裕延
Author(English)	Hironobu Oki
出典(和文)	学位:博士(理学), 学位授与機関:東京工業大学, 報告番号:甲第9407号, 授与年月日:2014年3月26日, 学位の種別:課程博士, 審査員:原　亨和,長井　圭治,柘植　丈治,北野　政明,野村　淳子
Citation(English)	Degree:Doctor (Science), Conferring organization: Tokyo Institute of Technology, Report number:甲第9407号, Conferred date:2014/3/26, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	論文要旨
Type(English)	Summary

（博士課程）
Doctoral Program

論 文 要 旨

THESIS SUMMARY

専攻： Department of	物質科学創造 専攻	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of （ 理学 ）
学生氏名： Student's Name	沖 裕延	指導教員（主）： Academic Advisor(main)	教授 原 亨和
		指導教員（副）： Academic Advisor(sub)	教授 神谷 利夫

要旨（英文 800 語程度）
Thesis Summary（approx.800 English Words ）

In this thesis, I studied environmentally benign production of industrially important ester polymers by using some solid acid catalysts. This thesis consists of four chapters including general introduction (chapter 1) and conclusions (chapter 4).

Chapter 1: General introduction

Esterification is one of the most important reactions in chemical industry for the production of plastics and polymers. Homogeneous acids, such as H_2SO_4 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 chapter, I described structure and unique catalysis of representative solid Brønsted acid catalyst.

Chapter 2: Synthesis of polyesterpolyol using MoO_3/ZrO_2

2.1 EXPERIMENTS

MoO_3/ZrO_2 (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 673 K ~ 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 ($Nb_2O_5 \cdot nH_2O$, Companhia Brasileira de Metalurgia e Mineração), H-beta (Zeolite, HSZ-940HOA, Tosoh), H-mordenite (Zeolite, HSZ-640HOA, Tosoh), and sulfated zirconia (SO_4^{2-}/ZrO_2, 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

MoO_3/ZrO_2 was composed of tetragonal and monoclinic ZrO_2, and hexagonal $ZrMo_2O_8$. Acid site density and the acid strength (H_0) of the MoO_3/ZrO_2 were estimated by NH_3 temperature-programming desorption analysis to be 0.16 mmol g^{-1} and ca. -13, respectively. MoO_3/ZrO_2 exhibits high catalytic performance for the polyesterification of 1.4-butanediol and adipic acid, whereas other solid acids, such as $Nb_2O_5 \cdot nH_2O$, zeolites, and SO_4^{2-}/ZrO_2, are not effective for the reaction. After reaction, the MoO_3/ZrO_2 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 the detection limit, which restricts degradation of the polymer with atmospheric water by hydrolysis. 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 MoO_3/ZrO_2 surface with reactant molecules Appropriate acid strength on MoO_3/ZrO_2 results in high catalysis for polyesterification of adipic acid with 1,4-butanediol.

Chapter 3: Acryloylation of hyperbranched polyetherpolyol using sulfonated carbon solid acid

3.1 EXPERIMENTS

Sulfonated carbon solid acid (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.

Hyperbranched multifunctional acrylate was synthesized by esterification of hyperbranched polyetherpolyol with acrylic acid. 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. 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 DAIAION 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 m^2 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 large amounts of SO_3H groups inside carbon bulk, which results in high catalytic performance. In the case of DAIAION, the reaction proceeds only on SO_3H groups on outer surface with small surface area. Because of small amounts of effective SO_3H groups, DAIAION shows no or poor catalysis.

Chapter 4 General conclusion

I briefly summarized chapter 2 and 3 in chapter 4.

備考 ： 論文要旨は、和文 2000 字と英文 300 語を 1 部ずつ提出するか、もしくは英文 800 語を 1 部提出してください。

Note : Thesis Summary should be submitted in either a copy of 2000 Japanese Characters and 300 Words (English) or 1copy of 800 Words (English).