

메조세공 BEA에 고정화된 키랄 Co살렌 착체의 동적분할을 통한 고광학순도의 키랄 모노에스테르 합성

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Synthesis of Optically Active Monoesters via Kinetic Resolution by Chiral Co (Salen) Complex Immobilized on Mesoporous BEA

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초 록

BEA형 제올라이트를 알칼리용액으로 처리하여 결정구조 내에 메조세공이 형성되도록 제조하고, 세공 내에 균일하게 키랄 Co(III) 살렌을 고정화시켰다. 메조세공 BEA-제올라이트에 고정화된 이핵형 Co-GaCl₃ 살렌 촉매는 말단 에폭사이드의 산소고리를 카르복실산으로 여는 키랄 반응에 대하여 높은 활성을 나타내었다. 이 반응을 통하여 라세믹 에폭사이드로부터 다양한 모노 에스테르 유도체를 중간 정도의 광학선택도(47~69 ee%)로 합성할 수 있었다. 키랄 (S)-ECH를 반응물로 사용하면, 이들은 키랄 살렌 촉매 존재하에서 카르복시 산에 의하여 에폭사이드의 링이 광학선택적으로 열리며, 생성된 화합물을 염기용액에서 탈염산 처리하면 다시 에폭사이드 링이 형성되면서 광학순도가 매우 높은 모노에스테르 에폭사이드 (R)-GB (98 ee% 이상)가 얻어졌다. 고정화촉매는 매우 용이하게 제조될 수 있었으며, 특별한 재생처리 없이 여러번 재사용하여도 촉매의 활성이 유지되었다.

Abstract

BEA-zeolite was modified by alkaline solution to introduce mesoporosity in the crystals and the homogeneous chiral Co(III) salen was immobilized in the mesopores. The dinuclear chiral Co(salen)-GaCl₃ catalyst immobilized on mesoporous BEA-zeolite showed high activity for the regioselective ring opening of terminal epoxides by carboxylic acids. Various chiral monoester derivatives could be synthesized with moderate enantioselectivity (47~69 ee%) from racemic epoxides through above reaction. When the chiral (S)-ECH was used as a reactant, it was efficiently resolved by carboxylic acid with a high enantioselectivity in the presence of heterogenized chiral salen catalyst, and the ring opened product afforded optically pure monoester epoxide (R)-GB (up to 98 ee%) through the ring closing in the basic solution by elimination of HCl. The heterogeneous catalyst could be fabricated easily, and the catalytic activity was retained for several times reuse without any further regeneration step.

Keywords: chiral salen, immobilization, mesoporous BEA-zeolite, glycidyl butylate, nucleophile

1. Introduction

The large academic and industrial interests have been focused on the stereoselective synthesis of chiral epoxides due to their versatile utility as intermediates for the preparation of bioactive molecules[1]. Therefore, the development in the preparation methods of optically pure terminal epoxides has been one of the important targets in the

asymmetric synthesis[2]. The catalytic ring opening of terminal epoxides provided a very efficient way in practical manner for the synthesis of optically enriched epoxides[3-5]. Among the myriads of nucleophiles that have been employed in the ring opening of epoxides, carboxylic acids could be catalyzed by chiral salen complexes, but they have been paid less attention until now[3,6]. The asymmetric ring opening (ARO) of meso epoxides using carboxylic acid as a nucleophile has been reported in the literature to obtain the chiral ester compounds[7]. The chiral glycidyl butyrate (GB) is known as one of the most valuable chiral intermediate for pharmaceutical drug production. This compound may be synthesized by the hydrolytic kinetic resolution of racemic GB in the presence of chiral salen catalysts. However chiral GB can be synthesized simply through the kinetic resolution of termi

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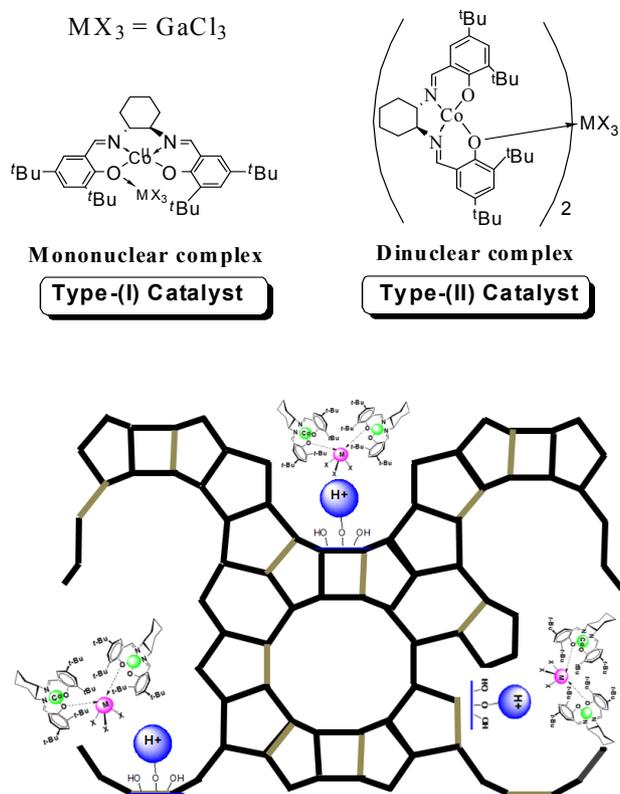


Figure 1. Representative structures of homogeneous salen complexes and those immobilized on mesoporous BEA-zeolite.

nal epoxides by carboxylic acid. It has been found that several systems based on the chiral Co(III) salen catalysts were very efficient for the highly enantioselective ring opening reaction of terminal epoxides[8]. These salen-based homogeneous catalysts have been appearing as excellent candidates for immobilization on the various supports. Heterogenized catalysts can offer many advantages in the facile separation of products with a simple recovery of catalysts for the practical application[9,10]. Various strategies have been explored to increase the catalytic efficiency of heterogenized salen catalysts. Some approaches were demonstrated successfully to date in the asymmetric catalysis by adopting the methodologies of adsorption, covalent bonding, as well as ship-in-bottle for immobilization of salen complexes[11-19].

The microporous zeolite crystal has been tested as a support to anchor the salen complexes having a simple structure[19-21]. However, the microscopic spaces in the zeolite pores are useless and restricted for the immobilization of large optically active salen molecules as mean of supports. Many types of heterogeneous salen catalysts have been developed by grafting on the inorganic material[15,16] or by copolymerization on the polymer[17,18] and by encapsulation in the pores[20,21]. The mesoporous material is an attractive support for heterogeneous catalysis application[1,10,15]. Until now, various kinds of microporous inorganic materials have been widely applied in the petrochemical industry. Especially among them, the zeolite crystals having very regular pore size were the most useful material for the separation and adsorption process through a molecular sieve action. Beta (BEA)

zeolites can provide both the large void spaces and more comfortable environment for guest molecules to trap the large molecules in micro-sized cages due to their bigger pore size, as compared to the others. Then, because the SiO_2/Al_2O_3 ratio of BEA zeolite is high as 10~20, the thermal and chemical resistances are excellent for use as adsorbent in the severe environment. However, microporous BEA zeolites have restricted small pores which are useless for immobilization of large molecules such as chiral salens in the pores. Their pore sizes are not efficient at processing of large molecules having meso-scale sizes. The development of simple method in the synthesis of zeolites with a regular shape mesopore or cage like pore channel remains as a challenging objective. Introducing the mesoporosity into zeolites has been examined by dealumination or desilication method via acid or alkaline post-treatment[20-22]. The larger void spaces in BEA zeolite can be formed by careful post-treatments through the selective extraction. This kind of mesoporous BEA zeolite may be applied as an attractive support for anchoring the big homogeneous salen complexes. In this work, a method to fabricate a novel mesoporous BEA zeolite with tunable pore size is presented, as well its application as a support for immobilization of chiral complexes to use in the ARO reaction of epoxides with carboxylic acids is reported. We have recently found that the dinuclear complexes bearing Lewis acids such as Al and Ga salts were highly efficient for ARO of terminal epoxides with H_2O or HCl[8,23]. Encouraged by these results, we have extended the applicability of these new catalysts for ARO of terminal epoxides with carboxylic acids in our work. Herein, a route to immobilize the active chiral Co(III) salen complexes on mesoporous BEA zeolite was demonstrated. These heterogeneous chiral catalysts showed high activity and selectivity in ARO of terminal epoxides for the synthesis of valuable derivatives such as chiral GB.

2. Experimental

2.1. Fabrication of Mesoporous BEA Zeolite by Alkali Treatment

H-type BEA zeolite (VALFOR CP, PQ Co. H-type, Si/Al = 25) was treated with NaOH solution in different concentrations (0.2 N, 0.6 N and 0.9 N) at 60 °C for 1 h. Alkali-treated BEA zeolites were washed with deionized water to remove the remaining alkali compound, and the zeolite particles were recovered by filtration. They were dried at 100 °C in the oven for overnight.

2.2. Immobilization of Chiral Co(III) Salen Complexes on Mesoporous BEA and Catalytic Reaction

The homogeneous chiral salen was immobilized on BEA support as shown in Figure 1. The chiral salens having different structures were prepared by the procedure as reported in the previous papers[8,23]. Subsequently, two type of heterogenized Co(III) salen- $GaCl_3$ complexes were prepared by reacting H^+ type mesoporous BEA zeolite with Cl-containing salen partners in refluxing CH_2Cl_2 for 1 h (Figure 1). The dark brown solid was rinsed sequentially with CH_2Cl_2 and THF, and dried *in vacuo* to yield a heterogenized Co salen complex. The catalytic activities were evaluated mainly by using racemic

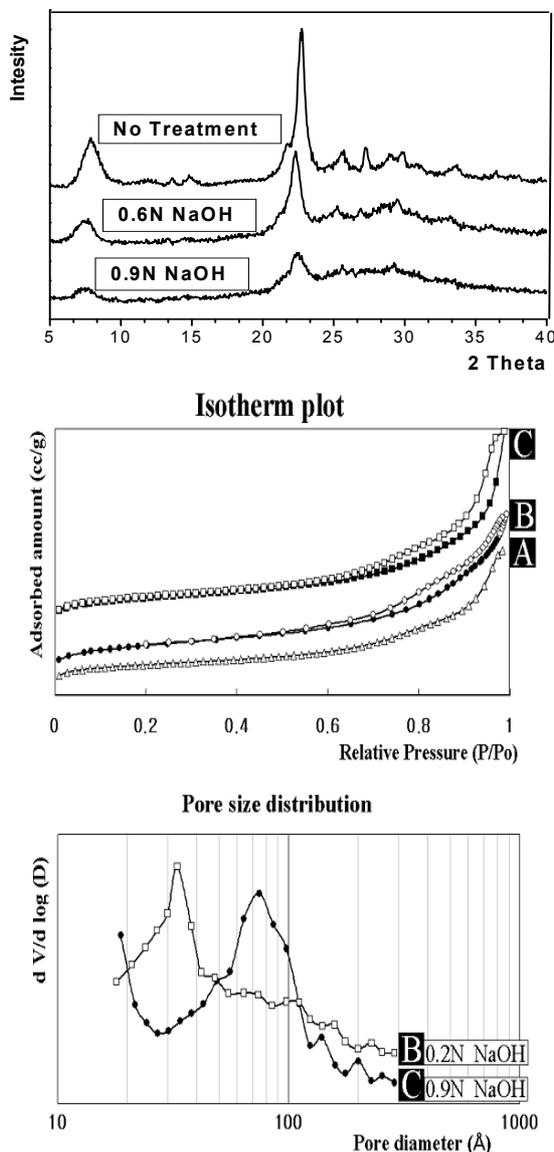


Figure 2. XRD patterns, N₂ adsorption/desorption isotherms and pore size distribution for original BEA-zeolite (A), and mesoporous BEA-zeolite post-treated by 0.2 N-NaOH (B), and 0.9 N-NaOH (C).

(±)epichlorohydrine ((±)ECH) or chiral (*R*)-ECH. In a representative reaction between ECH and carboxylic acid, the catalyst (3 mol% salen-loading/support), *tert*-butylmethylether (TBME; 10 mL) and (±)-ECH (10 mmol) were charged in 25 mL flask, and the reaction mixture was stirred in open atmosphere at the ambient temperature. After addition of carboxylic acid (5.5 mmol) as a nucleophile, the resultant mixture was stirred for 24 h. The conversion and enantiomeric excess% (ee%) values were determined by GC (CHIRALDEX (G-TA) and (A-TA), 20 m × 0.32 mm i.d. (Astech) capillary column) and HPLC (Chiralcel® OD column (24 cm × 0.46 cm i.d.; Chiral Technologies, Inc.) and (*R,R*)-Whelk-O1/(*S,S*)-Whelk-O1 column (24 cm × 0.46 cm i.d.) (Regis)).

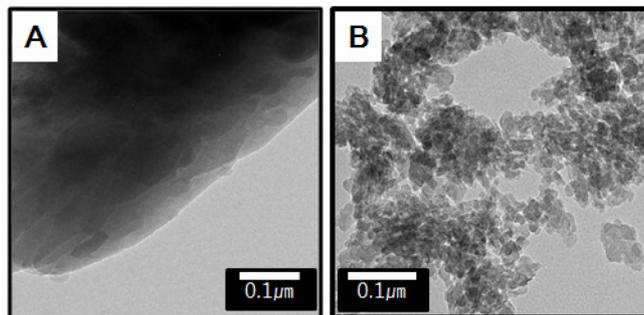


Figure 3. TEM image of fresh BEA-zeolite (A) and 0.6 N-NaOH treated mesoporous BEA-zeolite (B).

2.3. Characterization

The crystallinity of parent and treated BEA samples were characterized by X-ray diffractometer (Rigaku DMAX 2500). The formation of mesopores in BEA zeolite was confirmed by BET (ASAP 2000/Protech) adsorption analysis and field emission transmission electron microscopy (FE-TEM, S-4200). The nitrogen adsorption/desorption analysis was performed at -196 °C by using a surface area and porosity analyzing equipment (Micromeritics, ASAP 2010). The samples were out-gassed at 10⁻⁵ torr at 200 °C prior to measurement. The specific surface areas were calculated according to BET theory. The pore size was determined by BJH analysis. The Si/Al molar ratios of NaOH treated zeolites were determined from the contents of silica and alumina in the sample by EDX (Hitachi S-4200) analysis.

3. Results and Discussion

X-ray diffraction analysis was carried out to investigate the changes in BEA crystal structures during the alkaline treatment. Alkaline-treated BEA zeolite showed clear changes in diffraction patterns as compared to the parent BEA zeolite as shown in Figure 2. The intensity of peaks became decreased after treatment of NaOH solution, which implies a partial destroy in a crystal lattice. Characteristic diffraction peaks for BEA zeolite were decreased gradually with the increase of alkaline concentration for treatment. The yield of BEA zeolite recovered after post-treatment of 0.6 N-NaOH solution was 75%. As the NaOH concentration was increased, the recovered yield of zeolite sample was also decreased, because of the simultaneous dissolution of silica and alumina. The diffraction peaks for BEA was still exhibited on the x-ray diffractogram after 0.9 N-NaOH treatment, but its peak intensities were reduced as half of original sample, as can be seen in Figure 2. The Si/Al molar ratio of BEA sample was slightly decreased from 25 to 20 by 0.6 N-NaOH treatment, indicating a relatively higher solubility of silica than that of alumina during the alkali treatment.

To investigate the pore structure of BEA zeolite after alkali-treatment, nitrogen adsorption/desorption experiment was performed, and the isotherms for parent BEA zeolite and those of NaOH-treated BEA zeolite are listed in Figure 2. The fresh BEA zeolites showed Langmuir type I isotherm, indicating they have only the micropores in the matrix. Whereas, the isotherms for alkali-treated BEA zeolite sample exhibited

Table 1. Asymmetric Ring Opening of Racemic Terminal Epoxides with Various Carboxylic Acids Using Type-(II) Chiral Salen Catalyst Immobilized on Mesoporous BEA Zeolite

Entry	Epoxide (R)	Carboxylic Acid (R')	Catalyst (mole%)	Time (h)	Product ^a (ee%)
1	CH ₃		3.0	12	47
2	CH ₂ Br		4.0	12	54
3	CH ₂ Cl		4.0	10	56
4	CH ₂ Cl		4.0	10	59
5	C ₆ H ₄ OCH ₂		4.0	12	51
6	CH ₃		3.0	12	56
7	CH ₂ Cl		4.0	12	69
8	C ₂ H ₅		3.0	9	59
9	CH ₂ Cl		4.0	9	64

the characteristic hysteresis at high relative pressure(P/P₀). This result indicates that micro/meso-scopical bimodal pore system was generated in BEA crystals after post-treatment by NaOH solution. For BEA zeolites treated by NaOH solution of 0.6 N and 0.9 N, the shapes of hysteresis loops were indicative of type IV, which were generally obtained with adsorbents having slit-shaped or cage-like pores. The mean pore sizes of mesopores formed inside of BEA zeolite were estimated as 3.4 nm and 7.5 nm after post-treatment by 0.2 N and 0.9 N-NaOH, respectively.

FE-TEM images of BEA samples are shown in Figure 3. TEM photograph of BEA zeolite treated with 0.6 N-NaOH (Figure 3B) displays the presence of irregular mesopores penetrating the entire crystals. However, the mesoporosity was not observed on the starting microporous BEA crystals as shown in Figure 3A. It is clear that the mesopores were induced in the microporous BEA crystals through the dissolution of silica and alumina through the alkaline treatment (Figure 3B). The void volumes between the nano-crystals were increased as the concentration of NaOH solution was increased from 0.2 N to 0.9 N under the same treatment conditions. This mesoporous material was used successfully as a support to combine the chiral salen complexes after hydronium-ion exchange. Because the chlorine groups in the Co salen molecules were easily combined to the acid sites on the support, Na-type BEA zeolites formed after NaOH treatment were ion-exchanged to H-type.

The catalytic activities of immobilized chiral salen complexes for ARO of terminal epoxides with carboxylic acid are summarized in Table 1. Because the homogeneous salen complex of type-II was identified as most efficient and active one in the preliminary screening test, this type-II complex was chosen as a candidate for the preparation of heterogenized catalyst in further study. It is obvious from Table 1 that type-(II) catalyst immobilized on the mesoporous BEA zeolite showed

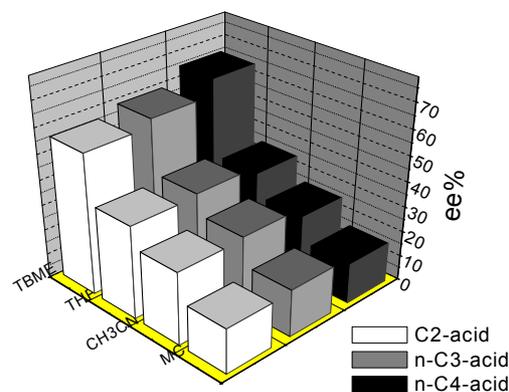


Figure 4. Effect of solvent type on products ee %'s in the reaction between the racemic ECH and n-carboxylic acids (TBME solvent, type(II) cata.; 3 mol%).

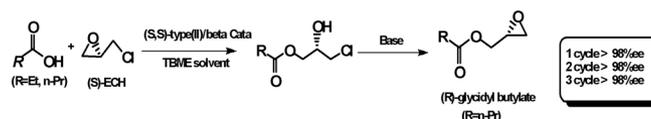


Figure 5. Recyclability of immobilized salen catalysts in the regioselective ring opening of (S)-ECH with carboxylic acids.

relatively high enantioselectivity (47-69 ee%) in the ARO of racemic epoxides. For all cases examined in this work, the conversion to the corresponding monoesters underwent highly within 24 h. However, for the heterogenized catalyst in comparison to the unsupported homogeneous one, the prolonged reaction time was required to reach the highest conversion level of epoxides for the synthesis of chiral monoester compounds.

To investigate the effects of solvents on the catalytic activities, various polar or non-polar organic compounds were used as a solvent in ARO reaction of terminal epoxides by carboxylic acids. Non-polar solvent such as TBME gave dramatically increased enantioselectivity to the products. The effects of solvent on the enantioselectivity in the reaction are shown in Figure 4. The heterogeneous type-(II) Co salen catalyst showed the almost same activity and enantioselectivity as homogeneous one in the reaction. When the different carboxylic acids, such as propionic acid and butyric acid, were used as nucleophiles, similar solvent effects on the catalytic activity and enantioselectivity were observed. This immobilized type-(II) catalyst was not only stable in the acidic media, but also recoverable by simple filtration and solvent rinse after termination of reactions.

In addition, the regioselective ring opening of chiral epoxides can be accomplished with carboxylic acids in the presence of heterogenized type-(II) salen catalysts, as shown in Figure 5. By the reaction between optically pure (S)-ECH and butyric acid, the ring opened product exhibited very high chirality. (R)-GB is known as a very important compound and has been used to introduce a stereogenic center in the synthesis of Linezolid which is currently marketed for the treatment of multidrug resistant Gram-positive infections. The GB product obtained by ring closing in the presence of base after ARO reaction has afforded an optically enriched GB with >98 ee% in quantitative yield. As

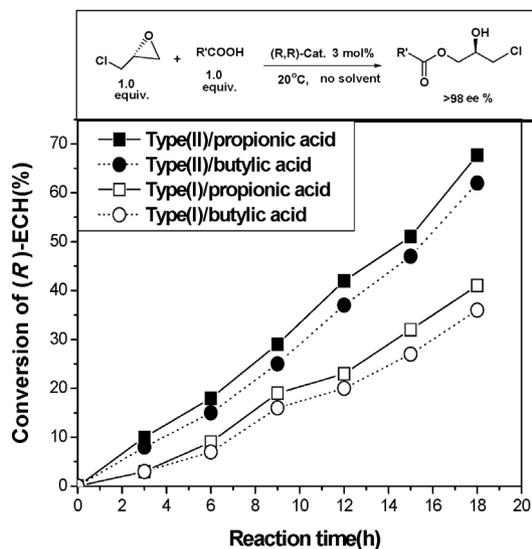


Figure 6. Comparison of the catalytic activity of salen complexes immobilized on mesoporous BEA zeolite in the ARO reaction between (R)-ECH and propionic acid or butyric acid.

a result, it was possible to obtain (R)-GB having high optical purity using type-II chiral salen catalysts immobilized on BEA zeolite in a simple manner. The heterogenized salen catalysts showed the excellent practical applicability for the repeated use to synthesize chiral (R)-GB by the reaction between (S)-ECH and butylic acid, followed HCl elimination in the presence of bases.

As shown in Figure 6, the higher catalytic activity was obtained by type-(II) heterogeneous catalyst than type-(I) in the regioselective ring opening of chiral (R)-ECH with carboxylic acids under the same conditions. The differences in the catalytic activities by using C3 and C4 carboxylic acids were not severe, showing the almost similar reaction rates and selectivity. However, when the propionic acid was used as a nucleophile for the ring opening of (R)-ECH, a slightly improved reaction rate was observed over both the type-(I) and (II) catalyst.

Cobalt ion-exchanged zeolite itself showed no activity in this reaction. In addition, the loading amount of salen on the original microporous BEA zeolite was so small that immobilization of salen catalyst on the parent BEA could be ignored. As can be expected, that sample exhibited no catalytic activity at all in the ARO reactions. As a result, it can be emphasize that the high catalytic activity in ARO reaction was generated wholly by the chiral salen catalysts immobilized inside the mesopores of BEA zeolite. It was clear that the bulky chiral salen complexes (15 Å in size) were mainly encapsulated in the mesopores of BEA not on the outer surfaces of microporous zeolite.

4. Conclusions

We have synthesized homogeneous and heterogeneous chiral dinuclear complexes and demonstrated their catalytic activity and selectivity for ARO of terminal epoxides with carboxylic acid as a nucleophile.

In addition, H-BEA-zeolite was modified by alkaline solution to introduce mesoporosity inside the crystals, and the chiral Co(III) salen was immobilized in the mesopores to obtain the heterogenized catalysts. The new heterogeneous dinuclear chiral Co salen catalyst (Type-II) immobilized on mesoporous BEA zeolite showed a high activity for the regioselective ring opening of terminal epoxides with carboxylic acids. Various chiral monoester derivatives could be synthesized with moderate enantioselectivity (47~69 ee%) from racemic epoxides via above reactions. The resolved ring opened product combined with ring closing in the presence of base has afforded optically pure epoxides such as (R)-GB in a quantitative yield with high ee% on the immobilized chiral salen catalyst by using chiral (S)-ECH as a reactant. The heterogeneous catalyst could be synthesized easily, and the catalytic activity was retained for several times reuse without any further regeneration step.

Acknowledgments

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