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Article

Immobilized 2,2,6,6-tetramethyl-piperidinyl-1-oxy catalyst on polymer microspheres and its catalytic oxidation of benzyl alcohol with molecular oxygen

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ABSTRACT

Crosslinked polymer (glycidyl methacrylate) microspheres (CPGMA) were prepared with glycidyl methacrylate as monomer and ethylene dimethacrylate as crosslinker by suspension polymerization. The ring opening reaction between the epoxy groups on the CPGMA microspheres and 4-hydroxy-2,2,6,6-tetramethyl-piperidinyl-1-oxy (4-OH-TEMPO) was carried out to immobilize TEMPO on the polymer microspheres. TEMPO-immobilized microspheres (TEMPO/CPGMA) were obtained and were characterized by several methods. The effects of the main factors in the immobilization were examined so that the reaction conditions were optimized. On this basis, a co-catalyst system was constituted with TEMPO/CPGMA and CuCl and was used in the oxidation reaction of benzyl alcohol by molecular oxygen. The catalytic activity of the co-catalyst system and the effects of the main factors were examined. The experimental results showed that the ring opening reaction of the epoxy group allowed the immobilization of TEMPO to be smoothly realized on the CPGMA polymer microspheres, on which there were many epoxy groups. The ring opening reaction of the epoxy group is a nucleophilic substitution reaction with the S_N2 reaction mechanism, and *N*,*N*′-dimethyl formamide with a strong polarity is an appropriate solvent and a suitable temperature is 85 °C. The co-catalyst system consisting of the heterogeneous catalyst TEMPO/CPGMA and CuCl efficiently catalyzed the oxidation reaction of benzyl alcohol by molecular oxygen. Under mild conditions, benzyl alcohol was transformed to benzaldehyde with 100% selectivity and a yield of 90%. The suitable molar ratio of the main catalyst TEMPO/CPGMA to the co-catalyst CuCl is 1:1.2 and the suitable amount of TEMPO/CPGMA is 0.90 g. The TEMPO/CPGMA catalyst has excellent recyclability.

1. Introduction

The oxidation of alcohols to carbonyl compounds is one of the most important chemical transformations in organic synthesis. Traditionally, the oxidation is accomplished by stoichiometric and strong oxidants (CrO_3, $KMnO_4$, MnO_2, etc.), which have a number of disadvantages, such as harsh reaction conditions, large amounts of waste that pollute the environment, and high cost of oxidants [1–4]. Green environmental protection and high atom economy are required in today's chemical processes, but the traditional transformations cannot meet these requirements. Therefore, it is necessary to develop a highly efficient and environment friendly oxidation process of alcohols to carbonyl compounds, in which a catalyst with high performance is very important. Besides heteropolyacids and metalloporphyrins [5,6], nitroxide free radicals are highly efficient

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catalysts for the oxidation of alcohol. Among the nitroxide free radicals, 2,2,6,6-tetramethyl-piperidinyl-1-oxy (TEMPO) has attracted much attention as a homogeneous catalyst. First, TEMPO is readily converted into a nitrogen carbonyl cation by a single electron oxidation, after which the nitrogen carbonyl cation, as a strong oxidant, enables primary and secondary alcohols to be quickly oxidized into the corresponding aldehyde or ketone with high conversion rate and high selectivity [7–10]. Also, by using TEMPO as the catalyst, the oxidation of alcohols can be carried out under mild conditions and with environment friendly oxidants, such as hydrogen peroxide and molecular oxygen [11–17]. Therefore, the use of TEMPO as the catalyst can achieve green synthesis. Moreover, the TEMPO catalyst has high stability because of the strong steric hindrance around the nitrogen groups [15].

Although TEMPO as a homogeneous catalyst exhibits good catalytic activity and selectivity, it is difficult to separate and recover TEMPO after the reaction, which severely restricts the development of the catalyst system. Immobilized TEMPO catalysts (heterogeneous TEMPO catalyst) on solid supports can overcome this shortcoming, and it also has some new catalytic characteristics, such as higher activity and is active without a co-catalyst [10,18]. The immobilization of TEMPO is one of the most important subjects in the study of catalytic oxidation. TEMPO has been immobilized on various solid supports, including silica gel, molecular sieves, and polymeric resins [19–21]. Among these supports, the polymer resin has received much attention as it is easy to introduce active groups on it by means of chemical modification, which facilitate the chemical bonding of TEMPO on these resins. For instance, researchers have prepared immobilized TEMPO catalyst by the bonding reaction between 4-hydroxy-2,2,6,6-tetramethyl-piperidinyl-1-oxy (4-OH-TEMPO) and the groups on the polymeric carriers, including carboxyl groups (or anhydride groups) and halide alkyl groups [22–24].

In our present investigation, crosslinked polymer (glycidyl methacrylate) (CPGMA) microspheres were first prepared by suspension polymerization. Then TEMPO was immobilized on the CPGMA microspheres by the ring opening reaction between 4-OH-TEMPO and epoxy groups on the CPGMA microspheres, and a novel TEMPO/CPGMA heterogeneous catalyst was thus obtained. TEMPO/CPGMA was used as the heterogenous catalyst for the oxidation of benzyl alcohol with molecular oxygen as an oxygen source. TEMPO/CPGMA exhibited high catalytic activity and excellent selectivity, and effectively transformed benzyl alcohol into benzaldehyde at room temperature. The mechanism of the heterogeneous catalytic oxidation reaction was explored.

2. Experimental

2.1. Preparation of crosslinked microspheres CPGMA

The crosslinked microspheres were prepared by suspension copolymerization of glycidyl methacrylate (GMA, AR grade, purchased from Nanhang Chemical Ltd, Suzhou, China, and purified by distillation under vacuum) and ethylene dimethacrylate (EGDMA, Industrial grade, obtained from Kaihua Chemical Limited Company, Yantai, China, and purified by distillation under vacuum) with azoisobutyronitrile (AR grade, purchased from Shanghai Chemical Reagent Plant, Shanghai, China, and recrystallized by standard procedures) as initiator. The continuous phase consisted of 50 mL distilled water containing 0.50 g polyvinyl alcohol (reagent grade, purchased from Sanwei Chemical Plant, degree of polymerization = 1799, Shanxi, China) and 3.50 g NaCl, which were used as dispersant and suspension stabilizer. The continuous phase was placed in a four-necked flask equipped with a mechanical stirrer, N_2 inlet, and a condenser. GMA (10.0 mL) was mixed with 1.0 mL EGDMA as the oil phase, which was used as the dispersed phase. The dispersed phase was added dropwise into the continuous phase slowly. The agitating speed was adjusted and the reaction mixture was stirred for 30 min at 45 °C to ensure good mixing of the two phases. The reactor was placed in a thermostat water bath, and when the mixture temperature was 55 °C, the initiator (0.10 g) was added, and under a nitrogen atmosphere, the copolymerization was carried out at 55 °C for 5 h. After the reaction, the microspheres were filtered off and washed with distilled water and ethanol in turn. Finally, the product was dried under vacuum at 50 °C, and white translucent crosslinked GMA/EGDMA microspheres were obtained. Because GMA was the main monomer, they were named CPGMA.

2.2. Preparation of immobilized microspheres TEMPO/CPGMA

CPGMA microspheres were placed in a four-necked flask equipped with a mechanical stirrer, N_2 inlet, and a condenser, followed by adding *N*,*N*′-dimethyl formamide (DMF, AR grade, purchased from Tientsin Dibo Chemical Reagent Plant, Tianjin, China) as solvent. The microspheres were soaked and swelled for 12 h. 4-OH-TEMPO (2.14 g, chemically pure, supplied from Ruishuo Chemical Limited Company, Shanghai, China) were dissolved in 30 mL of DMF, and the mixture was added into the four-necked flask. After that, a saturated Na_2CO_3 solution (5 mL) as catalyst was added into the reaction system. The quaternization reaction was carried out for 12 h at 85 °C under N_2 atmosphere. After ending the reaction, the final product microspheres were collected by filtering. Then they were washed with water and ethanol in turn several times. Finally they were dried under vacuum at 50 °C to a constant weight, and the immobilized TEMPO complex catalyst (designated as TEMPO/CPGMA) was gained. Furthermore, by varying the feed ratio, the reaction temperature, and the solvent, the effects of these factors on the immobilized reaction were examined.

2.3. Characterization of catalysts

The chemical structure of the crosslinked microbeads CPGMA and immobilized TEMPO/CPGMA microspheres were characterized by FT-IR (Perkin-Elmer 1700 infrared spectrometer, Perkin-Elmer Company, USA). Their morphology and size (particle diameter) were characterized by scanning electron microscopy (SEM, 438VP scanning electron microscopy, LEO company, UK) and an optical microscope (XSZ-4 optical microscope with micrometer, Taiyuan Optics Instrument Factory, China). The amount of epoxy groups on the CPGMA was calculated from the monomer feed ratio (6.17 mmol/g). The amount of epoxy groups on the TEMPO/CPGMA surface was determined by the pyridine-hydrochloride method [25], and the immobilized amount (mmol/g) of TEMPO was calculated. The immobilized TEMPO/CPGMA catalysts used in this study have an immobilized amount of 3.14 mmol/g.

2.4. Catalytic oxidation of benzyl alcohol with molecular oxygen

Benzyl alcohol (5 mL, AR grade, Guoyao Chemicals Co. Ltd., Beijing, China) and 50 mL of DMF as solvent were placed into a reactor equipped with a mechanical stirrer, a reflux condenser, a thermometer, and an O_2 inlet, followed by adding 0.90 g of TEMPO/CPGMA microspheres and 0.242 g of CuCl. Oxygen at normal pressure was passed into the mixture at a fixed flow rate (15 mL/min). The oxidation reaction was performed at 25 °C with stirring for 20 h. Samples of the reaction mixture were taken at fixed time intervals, and the analysis was carried out immediately by gas chromatography (GC) with the area-normalization standard method (N_2, HP-5 capillary column, FID detector). The GC analysis indicated that benzaldehyde was the only product, showing that this catalytic oxidation system has excellent selectivity. The benzaldehyde yield and conversion of benzyl alcohol were calculated from the GC data. After finishing the reaction, the TEMPO/CPGMA microspheres were collected by filtration, and washed alternately with DMF and ethanol. In order to remove adsorbed molecules on the catalyst, the microspheres were soaked in ammonia for 12 h and then washed with distilled water. After drying under vacuum to a constant weight, TEMPO/CPGMA was obtained for recycling.

In order to examine the effects of the main factors on the catalytic oxidation reaction and to optimize the reaction conditions, the molar ratio of main catalyst and co-catalyst, used amount of the solid catalyst, reaction temperature, and solvent were changed in turn, and the catalytic oxidation of benzyl alcohol was carried out under the different conditions.

3. Results and discussion

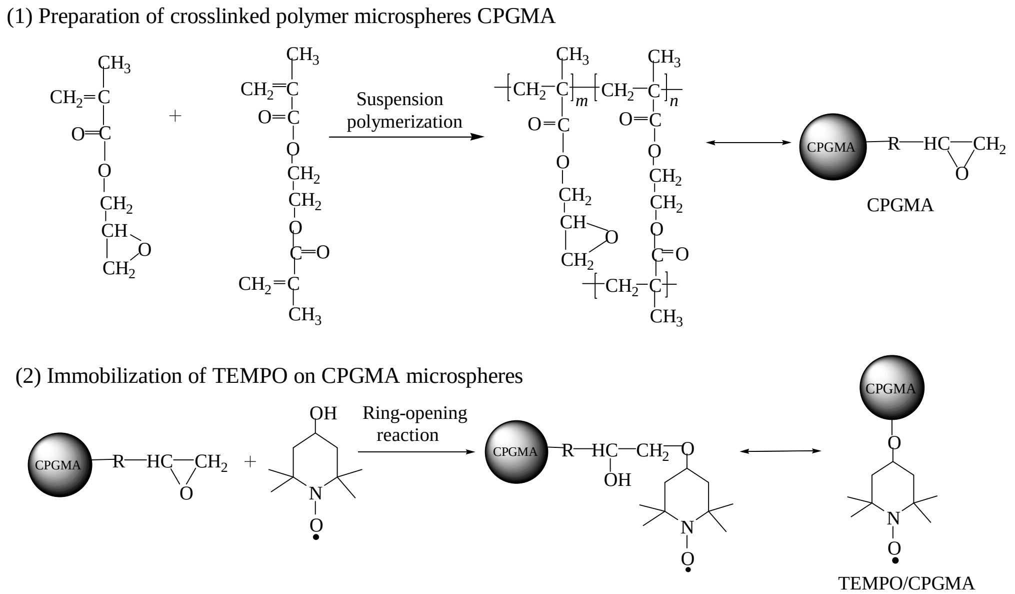
3.1. Preparation of immobilized TEMPO complex catalyst TEMPO/CPGMA

In this work, molecular design was used to get free radicals immobilized on the surface of polymer microspheres containing epoxy groups. The crosslinked microspheres, CPGMA, were prepared by suspension copolymerization of GMA and EGDMA, and EGDMA was used as crosslinker. There are abundant epoxy groups on the surface of the CPGMA crosslinked microspheres. 4-OH-TEMPO can be easily bonded on the surface of the crosslinked microspheres by the ring opening reaction of the epoxy groups under alkaline condition. Thus, the immobilized TEMPO/CPGMA microspheres were formed. The process to prepare the immobilized TEMPO/CPGMA microspheres is demonstrated in Scheme 1.

3.2. Characterization of the crosslinked microspheres and immobilized microspheres

3.2.1. FT-IR spectra of the microspheres

Figure 1 gives the FT-IR spectra of the CPGMA and TEMPO/CPGMA microspheres. In the spectrum of CPGMA, the characteristic absorption band at 1731 cm^{-1} was attributed to the ester carbonyl groups of GMA and EGDMA. The characteristic absorption of the epoxide rings appeared at 906 and 844 cm^{-1}. The band at 2953 cm^{-1} is the stretching vibration absorption of the methylene groups of EGDMA and the main chain of the polymer. The band at 3000 cm^{-1} was ascribed to the stretching vibration absorption of the methyl groups of GMA. The appearances of these bands revealed that the crosslinked



Scheme 1. Chemistry of preparing the TEMPO/CPGMA heterogeneous catalyst.

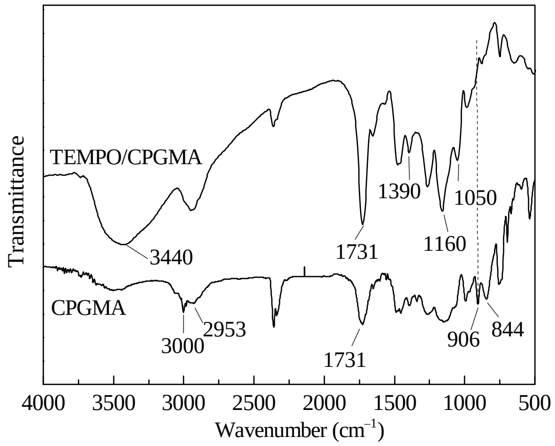


Fig. 1. FT-IR spectra of the two microspheres.

copolymerization of GMA and EGDMA has occurred, and crosslinked CPGMA microspheres were formed.

The FT-IR spectrum of TEMPO/CPGMA has some absorption bands different from those of the CPGMA crosslinked microspheres. In the spectrum of the TEMPO/CPGMA microspheres, the characteristic absorption bands of the epoxy groups at 906 and 844 cm^{-1} were much weakened, whereas the characteristic absorption band of the free radicals group N–O and ether group C–O–C appeared at 1390 and 1160 cm^{-1}, respectively. The strong absorption band at 3440 cm^{-1} representing the –OH stretching vibration absorption is due to 4-OH-TEMPO grafted onto the CPGMA crosslinked microspheres, which is a result of the ring opening reaction of epoxy. Therefore, the FT-IR spectrum data fully demonstrated that 4-OH-TEMPO was bonded onto the crosslinked CPGMA microspheres by the ring opening reaction of epoxy, and immobilized TEMPO/CPGMA microspheres were prepared.

3.2.2. Morphology of the microspheres

Figure 2 presents the SEM images of the crosslinked CPGMA microspheres and immobilized TEMPO/CPGMA microspheres. The CPGMA microspheres were more spherical and had a more uniform particle size. After the immobilization reaction, the immobilized TEMPO/CPGMA microspheres were still spherical, but the surface of the microspheres had became a little rough and scraggy, which was a result of the macromolecular reaction (ring opening reaction of epoxy groups) on the surface of the microspheres, indicating the immobilization of TEMPO on the microspheres.

3.3. Effects of main factors on the immobilization of TEMPO

3.3.1. Effect of reactant ratio

In the reaction system described in Section 2.2, with a fixed amount of CPGMA and volume of solvent, the reaction was carried out by changing the molar ratio of 4-OH-TEMPO to the epoxy groups on the microspheres. Figure 3 gives the curves of the immobilized amount (IA) of TEMPO versus time at different reactant ratios. With increasing molar ratio between 4-OH-TEMPO and epoxy groups on the microspheres, the immobilized amount of TEMPO increased rapidly. The ring opening reaction of epoxy groups and 4-OH-TEMPO is a nucleophilic substitution reaction with the S$_N$2 reaction mechanism because increasing the concentration of 4-OH-TEMPO, which was used as the nucleophilic reagent, accelerated the reaction rate, resulting in the increase amount of immobilized TEMPO. However, as the concentration increased beyond a certain value, the increase in immobilized amount began to slow down. As can be seen from Fig. 3, the curve of the reactant ratio of 1:2.0 is close to that with 1:3.0. For this system, an adequate reactant ratio should be selected as 1:2.0, with which the immobilized amount of TEMPO can reach 3.14 mmol/g.

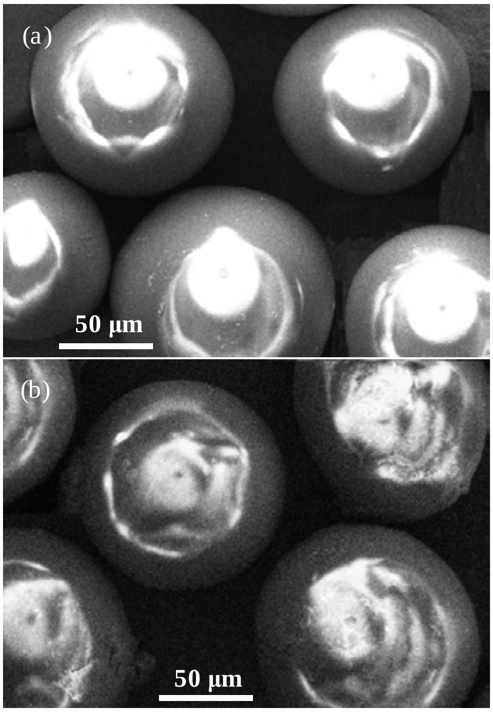


Fig. 2. SEM photographs of the CPGMA and TEMPO/CPGMA microspheres.

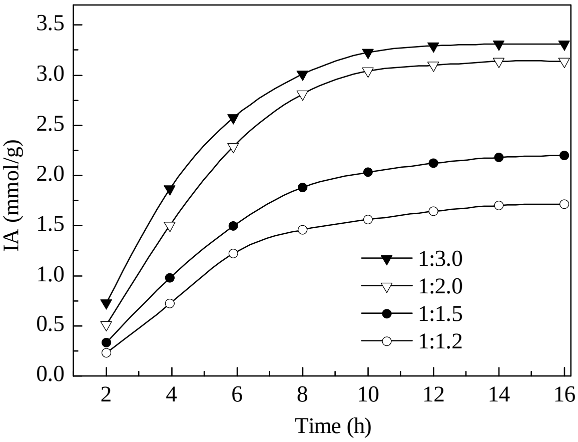


Fig. 3. Immobilized amount (IA) of TEMPO on TEMPO/CPGMA microspheres versus time at different 4-OH-TEMPO: epoxy groups ratios. Reaction conditions: DMF as solvent, 85 °C.

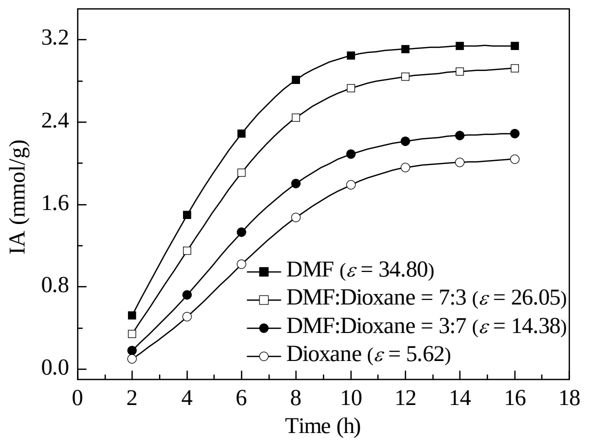


Fig. 4. TEMPO bonded amount obtained using different solvents. Reaction conditions: 85 °C, feed ratio 1:1.2. ε: Dielectric constants of the solvents at 25 °C, and the dielectric constant of the mixed solvent was calculated according to molar ratio of the two solvents.

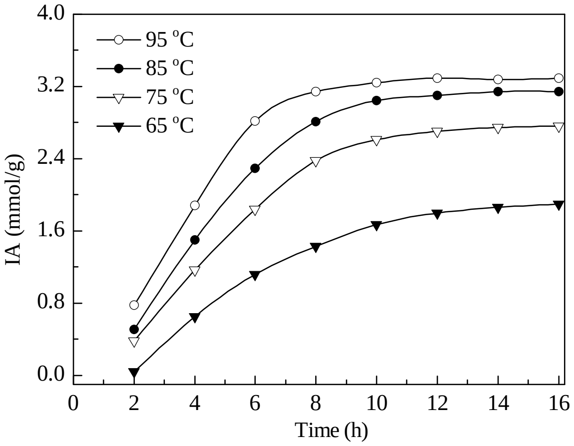


Fig. 5. TEMPO bonded amount obtained at different temperatures. Reaction conditions: DMF as solvent, feed ratio 1:1.2.

3.3.2. *Effect of solvent polarity*

By fixing the other reaction conditions, the ring opening reaction between epoxide groups and 4-OH-TEMPO was conducted using four solvents with different polarities and dielectric constants (ε): DMF, 1,4-dioxane, mixture of DMF and 1,4-dioxane (v/v = 7:3), and mixture of DMF and 1,4-dioxane (v/v = 3:7). Figure 4 presents the immobilized amount of TEMPO versus time using the different solvents.

The polarity of the four solvents was in the order of DMF > DMF + 1,4-dioxane (v/v = 7:3) > DMF + 1,4-dioxane (v/v = 3:7) > 1,4-dioxane. DMF was the best solvent, while 1,4-dioxane was the worst. This order is coincident with the polarity of the four solvents. That is, a higher solvent polarity gave more immobilized amount.

The solvent polarity has a large effect on the immobilization reaction. The possible reason for this is as follows. It was found by experiment that the four solvents have good swelling property on the crosslinked CPGMA microspheres, that is, the crosslinked network can be fully stretched, and the epoxy groups of the macromolecular chains and nucleophilic reagent have good contact with each other. A higher solvent polarity gives a stronger dipole-dipole interaction of solvent and nucleophilic reagent, which is helpful for removing the hydroxyl hydrogen protons and attacking the epoxy groups with 4-OH-TEMPO. Based on this, the nucleophilic substitution reaction is promoted, resulting in the enhancement of the immobilized amount. Therefore, DMF should be selected as a suitable solvent for this reaction.

3.3.3. *Effect of temperature*

By fixing the other reaction conditions, the immobilization reaction of TEMPO was performed with changing of the temperature of the ring opening reaction. Figure 5 gives the immobilized amount of TEMPO versus time at different temperatures. The results clearly showed that at lower temperatures, the immobilized amount was low due to the lower efficiency of the ring opening reaction. The reaction rate increased with temperature, resulting in higher immobilized amount of TEMPO in the same period of time. Because the immobilized amount of TEMPO at 85 °C was very close to that at 95 °C, a suitable reaction temperature is 85 °C.

3.4. *Catalytic characteristics of TEMPO/CPGMA in the oxidation of benzyl alcohol with molecular oxygen*

3.4.1. *Catalytic activity and mechanism*

The oxidation of benzyl alcohol was conducted in the following catalyst systems: (1) TEMPO/CPGMA and CuCl (molar ratio 1:1.2); (2) TEMPO/CPGMA; (3) CuCl; (4) without catalyst. In the above (1) and (2) catalyst systems, the immobilized amount of TEMPO on TEMPO/CPGMA was 3.14 mmol/g. Figure 6 gives the benzaldehyde yield versus time in the four systems. It indicates that the oxidation of benzyl alcohol nearly did not occur without catalyst. When some primary catalyst TEMPO/CAGMA or cocatalyst CuCl were introduced, benzaldehyde was produced with very low yield. For the co-catalyst system composed of TEMPO/CPGMA and CuCl, the yield of benzaldehyde was much enhanced, and it was up to 90% when the reaction time was 20 h. As compared to an immobilized TEMPO loaded on a molecular sieve and CuCl system (which

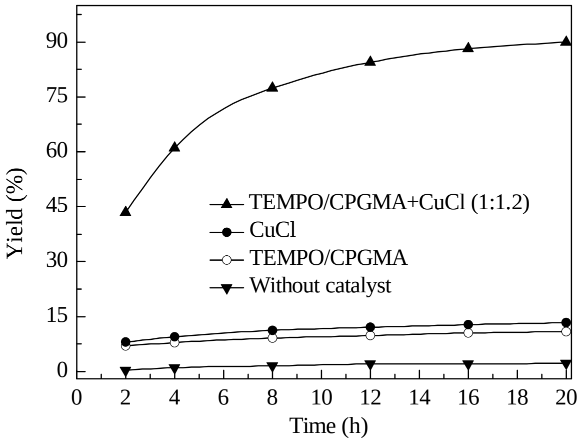


Fig. 6. Benzaldehyde yield with time using different catalyst systems. Reaction conditions: 25 °C, DMF as solvent, O_2 at atmospheric pressure.

gave after 48 h, the yield of benzaldehyde of 35%) reported previously [26], it is obvious that the co-catalyst system consisting of the immobilized TEMPO designed and prepared in this investigation and CuCl has a higher catalytic activity. This showed that the co-catalyst system consisting of TEMPO/CPGMA and CuCl is a highly effective catalyst system for the oxidation of primary alcohols to the corresponding aldehyde.

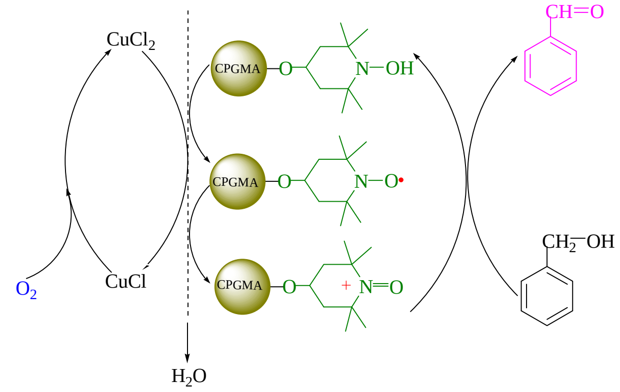
The oxidation of alcohols can be effectively catalyzed by the TEMPO catalyst, and the catalytic mechanism is the oxoaminium salt cation process [7,10,27], which is not a free radical reaction mechanism. In the oxidation of benzyl alcohol with the above co-catalyst system, the reaction mechanism is suggested as follows (Scheme 2): first, the co-catalyst CuCl is oxidized to Cu (II) under oxygen; then the one-electron oxidation of TEMPO takes place, and the oxoaminium salt cation with strong oxidizability is obtained; then the oxoaminium salt cation obtains hydrogen from benzyl alcohol under mild conditions, resulting in the highly effective oxidation of benzyl alcohol into benzaldehyde. At the same time, the catalyst is returned as the reduced TEMPOH, and one catalytic oxidation cycle is completed. Based on this catalytic mechanism without free radicals, the oxidation of benzyl alcohol into the corresponding carboxylic acid is avoided.

3.4.2. *Effect of added amount of CuCl on the catalytic oxidation reaction*

By fixing the other reaction conditions, the oxidation of benzyl alcohol was performed with changing of the dosage of the CuCl co-catalyst. Benzaldehyde yields versus time are shown in Fig. 7. Figure 7 shows that with an increase of added amount of CuCl, the benzaldehyde yield is increased. When the molar ratio of primary TEMPO catalyst and CuCl cocatalyst is 1:1.2, and the reaction time is 20 h, the benzaldehyde yield was about 90%. If the added amount of CuCl was further increased (TEMPO:CuCl = 1:1.5), the benzaldehyde yield was barely changed, i.e., too much CuCl no longer affects the oxidation reaction. Therefore, for this catalytic oxidation system, the proper molar ratio of primary catalyst to co-catalyst is 1:1.2.

3.4.3. *Effect of the amount of the catalytic system on the oxidation reaction*

The oxidation of benzyl alcohol was conducted using different amounts of TEMPO/CPGMA when the molar ratio of TEMPO and CuCl was 1:1.2 and the other reaction conditions were fixed. The yield of benzaldehyde with time is shown in Fig. 8. It can be found that the yield of benzaldehyde increased with increasing amount of TEMPO/CPGMA, which is in accord with the characteristics of the heterogeneous catalytic reaction. However, when the amount of TEMPO/CPGMA was increased to 0.90 g and the yield of benzaldehyde reached 90%, the increased yield with increasing amount of catalyst was very small. So for this reaction system, the suitable amount of TEMPO/CPGMA is 0.90 g (the molar ratio of TEMPO and CuCl is 1:1.2).



Scheme 2. Catalytic mechanisam of TEMPO/CPGMA+CuCl catalyst in the oxidation of benzyl alcohol to benzaldehyde by O_2.

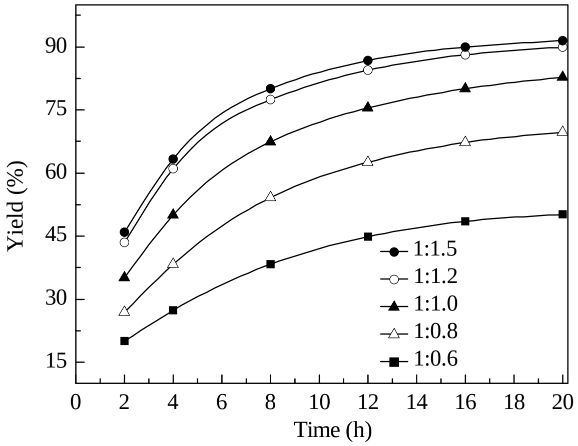


Fig. 7. Benzaldehyde yield with reaction time with different added amounts of CuCl. Reaction conditions: TEMPO/CPGMA is 0.90 g, DMF as solvent, 25 °C, O_2 at atmospheric pressure.

3.4.4. *Catalytic activity of reused TEMPO/CPGMA*

To investigate the catalytic activity of reused TEMPO/CPGMA, the supported catalyst used in each catalytic oxidation was separated from the reaction mixture for reuse. CuCl and TEMPO/CPGMA were used together as composite catalysts. The experimental results are shown in Fig. 9. During the reuse of 6 times, the catalytic activity declined a little at the second

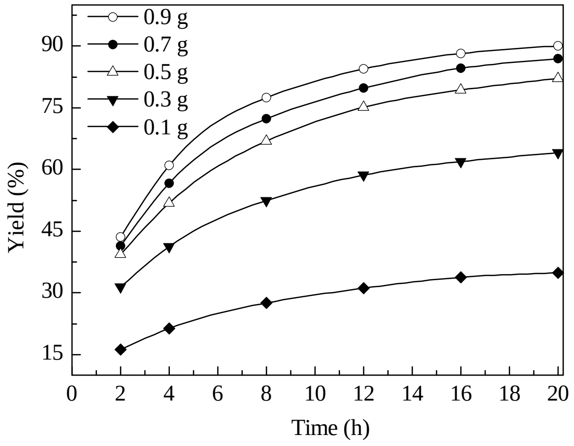


Fig. 8. Benzaldehyde yield with reaction time with different amounts of co-catalyst. Reaction conditions: 25 °C, DMF as solvent, main catalyst: sub-catalyst = 1:1.2, O_2 at atmospheric pressure.

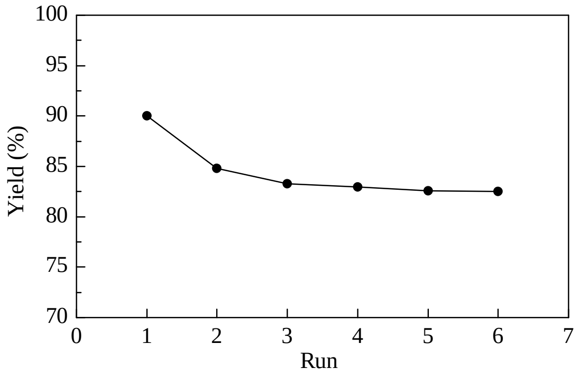


Fig. 9. Effect of cycle number on catalyst activity. Reaction conditions: TEMPO/CPGMA is 0.90 g, 25 °C, DMF as solvent, main catalyst: sub-catalyst = 1:1.2, O_2 at atmospheric pressure.

recycle (benzaldehyde yield fallen to 85% from 90%); after that, the catalytic activity was quite stable (benzaldehyde yield > 83%). In addition, the spherical shape of TEMPO/CPGMA was kept well during the recycling, and their appearance did not show any significant change. Therefore, it can be concluded that this immobilized catalyst has excellent reuse performance.

4. Conclusions

TEMPO-immobilized microspheres, TEMPO/CPGMA, were prepared by the ring opening reaction between the epoxy groups on the CPGMA microspheres and 4-OH-TEMPO, and were successfully applied in the oxidation reaction of benzyl alcohol using molecular oxygen. The ring opening reaction between the epoxy groups and 4-OH-TEMPO is a nucleophilic substitution reaction with the S_N2 reaction mechanism. DMF is an appropriate solvent and a suitable temperature is 85 °C. With a co-catalyst system consisting of TEMPO/CPGMA and CuCl, benzyl alcohol was transformed into benzaldehyde effectively and mildly. In the oxidation reaction of benzyl alcohol using molecular oxygen as an oxygen source, the co-catalyst system constituted by TEMPO/CPGMA and CuCl exhibited high catalytic activity, and effectively transformed benzyl alcohol to benzaldehyde as the sole product, displaying excellent selectivity at normal temperature and pressure (100% selectivity of benzaldehyde, 90% yield). The results showed that a suitable molar ratio of the TEMPO/CPGMA main catalyst to the CuCl co-catalyst is 1:1.2. The suitable amount of TEMPO/CPGMA main catalyst is 0.90 g. This immobilized catalyst TEMPO/CPGMA has excellent recycling and reuse property.

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Graphical Abstract

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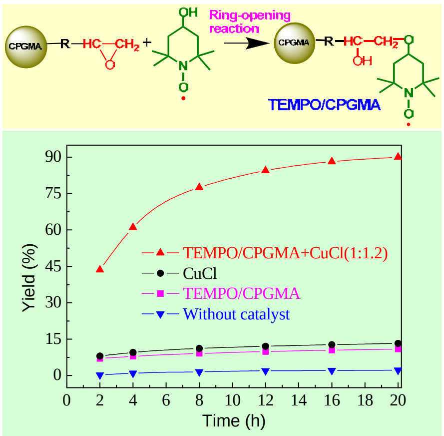
North University of China



2,2,6,6-Tetramethyl-piperidinyl-1-oxy (TEMPO) was successfully immobilized on crosslinked polymer microspheres containing epoxy groups by the ring opening reaction between the epoxy group on the polymer microspheres and 4-OH-TEMPO, giving immobilized TEMPO/CPGMA microspheres. A co-catalyst system of TEMPO/CPGMA and CuCl efficiently catalyzed the oxidation of benzyl alcohol to benzaldehyde under mild conditions.

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含环氧基团的聚合物微球固载2,2,6,6-四甲基哌啶氮氧自由基催化剂的制备及其催化分子氧氧化苯甲醇

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摘要: 以甲基丙烯酸缩水甘油酯(GMA)为单体，以乙二醇二甲基丙烯酸酯(EGDMA)为交联剂，采用悬浮聚合法制得交联聚甲基丙烯酸缩水甘油酯(CPGMA)微球，然后以4-羟基-2,2,6,6-四甲基哌啶氮氧自由基(4-OH-TEMPO)为试剂，使CPGMA微球表面的环氧基团发生开环反应，从而制得了TEMPO固载化微球TEMPO/CPGMA，考察了制备条件对固载化反应的影响，并采用多种方法对微球TEMPO/CPGMA进行了表征. 将微球TEMPO/CPGMA与CuCl组成共催化体系，用于分子氧氧化苯甲醇，考察了反应条件对催化体系性能的影响. 结果表明，以含环氧基团的聚合物微球CPGMA为载体，通过开环反应，可成功地实现TEMPO的固载化，开环反应属S_N2亲核取代反应，适宜采用溶剂*N*,*N*′-二甲基甲酰胺和反应温度85 °C. 非均相催化剂TEMPO/CPGMA与助催化剂CuCl构成共催化体系，在室温、常压O_2条件下可高效地将苯甲醇氧化为苯甲醛，产物选择性和产率分别为100%和90%. 主催化剂TEMPO与助催化剂CuCl适宜的摩尔比为1:1.2; 主催化剂适宜用量为0.90 g. 此外，TEMPO/CPGMA固体催化剂具有良好的循环使用性能.

关键词: 聚甲基丙烯酸缩水甘油酯; 氮氧自由基; 固载; 醇氧化; 分子氧

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1. 前言

醇氧化为羰基化合物是有机合成中最重要的化学转化之一, 在实验室研究和精细化工生产中都占有非常重要的地位. 该过程传统上需使用一些化学计量的强氧化剂如CrO_3, $KMnO_4$, MnO_2等, 存在着反应条件苛刻、产生大量废弃污染物、以及氧化剂成本高等不足[1–4]. 而当今的化工过程, 要求具有绿色环保性和高原子经济性, 显然, 上述传统的转变过程不适应这一要求. 因此, 需要大力发展高效环保的醇氧化过程, 其中高性能催化剂是关键. 除杂多酸及金属卟啉[5,6]等催化剂外, 氮氧自由基催化剂也是实现醇氧化的高效催化剂, 其中, 以均相的2,2,6,6-四甲基哌啶氮氧自由基(TEMPO)催化剂备受关注. TEMPO可通过单电子氧化过程转化为相应的氮羰基阳离子, 这是一个氧化性很强的氧化剂, 可将伯醇和仲醇快速高转化率、高选择性地氧化为对应的醛或酮[7–10], 还可以使用那些环境友好型氧化剂(如H_2O_2、分子氧等), 从而在温和条件下绿色化地实现醇的氧化转变[11–17], 而且由于氮氧基团周围强立体位阻, 使TEMPO催化剂具有高稳定性的特点[15].

作为均相催化剂, TEMPO虽然表现出良好的催化活性和选择性, 但反应后难以分离回收, 不能再循环使用, 严重制约着催化体系的应用. 将TEMPO化学键合在固体载体上, 实现TEMPO的固载化, 不但可克服上述缺点, 而且具有更高的活性以及免于使用助催化剂等特点 [10,18]. 因此, TEMPO的固载化成为目前催化氧化领域中一个重要的研究课题. 固载TEMPO的载体主要有硅胶、分子筛、聚合物树脂等[19–21], 其中, 由于聚合物材料易于通过化学修饰引入活性基团, 便于TEMPO的化学键合而备受注目. 例如, 分别以含有羧基(或酸酐基团)及卤烷基团的聚合物为载体(或载体前躯体), 通过与4-羟基-TEMPO (4-OH-TEMPO)发生键合反应, 制备了固载化的TEMPO催化剂[22–24].

到目前为止, 固载化TEMPO催化剂的报道还很少, 因此, 本文采用悬浮聚合法进行甲基丙烯酸缩水甘油酯(GMA)的交联聚合, 制得表面含有环氧基团的交联聚合物微球CPGMA; 然后利用环氧基团与4-OH-TEMPO的开环反应, 将TEMPO键合在微球表面, 制得非均相催化

剂TEMPO/CPGMA；并将其用于室温常压下分子氧氧化苯甲醇, 并研究非均相催化氧化反应的机理.

2. 实验部分

2.1. 交联微球CPGMA的制备

将0.50 g聚乙烯醇(聚合度1799, 山西三维化工有限公司)和3.50 g NaCl溶于50 mL蒸馏水中构成水相；将10 mL的单体GMA (AR, 苏州南航化工有限公司, 使用前经减压蒸馏提纯)和1 mL的交联剂乙二醇二甲基丙烯酸酯(EGDMA, AR, 山东烟台云开化工有限公司, 使用前进行减压蒸馏)相混溶, 构成油相. 在装有搅拌器、冷凝管、导气管的四口瓶中加入水相, 并加热至45 °C, 通入氮气30 min, 然后将油相缓慢滴加到水相中, 在恒温下搅拌30 min, 使其充分分散形成悬浮体系. 将体系温度升高到55 °C, 加入0.10 g的引发剂偶氮二异丁腈(AR, 上海化学试剂厂), 在氮气保护下恒温反应5 h, 反应结束后将微球滤出, 用乙醇和蒸馏水多次洗涤, 于50 °C下真空干燥至恒重, 即制得半透明状的白色交联聚合物(CP)微球GMA/EGDMA, 由于GMA是主单体, 故简写为CPGMA微球.

2.2. TEMPO在交联微球表面的固载化

称取1.0 g CPGMA微球置于装有搅拌器、冷凝管和导气管的四口瓶中, 加入20 mL的溶剂*N*,*N*′-二甲基甲酰胺(DMF, AR, 天津市博迪化工有限公司)使微球充分溶胀12 h. 再称取2.14 g 4-OH-TEMPO (CP, 上海瑞硕化工), 用30 mL的DMF溶解后加入到四口瓶中, 再加入5 mL饱和Na_2CO_3溶液, 将体系的温度升至85 °C, 恒温搅拌并在氮气保护下反应12 h. 反应结束后滤出微球, 用蒸馏水与无水乙醇反复多次洗涤, 于50 °C下真空干燥至恒重, 即得氮氧自由基固载化微球TEMPO/CPGMA. 同时, 考察反应温度、投料比、溶剂等主要因素对TEMPO固载化反应的影响.

2.3. 产物的表征

采用溴化钾压片法测定CPGMA微球和TEMPO/CPGMA微球的FT-IR(1700型傅里叶红外光谱仪, 美国Perkin-Elmer公司)谱, 对其化学结构进行表征；用生物显微镜(带有测微尺的XSZ-4型双目生物显微镜, 太原光学仪器厂)测定其粒径(约为100 μm)；用扫描电镜(SEM, 438VP型扫描电子显微镜, 英国LEO公司)观察其形貌. 交联微球上环氧基团的含量以单体投料比求得约为6.17 mmol/g. 采用吡啶-盐酸法[25], 测定微球TEMPO/CPGMA表面环氧基团的剩余量, 从而测得TEMPO的固载量(IA)为3.14 mmol/g.

2.4. 苯甲醇的分子氧催化氧化

在装有搅拌器及冷凝回流管装置的四口烧瓶中, 加入50 mL DMF和5 mL苯甲醇, 再加入0.90 g固载化微球TEMPO/CPGMA及0.242 g助催化剂CuCl, 常压下以恒定的流速通入O_2 (15 mL/min), 搅拌下于25 °C恒温反应20 h. 间隔一定时间取样, 用气相色谱仪分析产物(N_2气为载气, HP-5毛细管色谱柱, FID检测). 分析结果表明, 产物苯甲醛是唯一的产物. 反应结束后, 抽滤收集固体催化剂, 先用DMF和乙醇反复洗涤, 洗涤至滤液中无产物苯甲醛的紫外特征吸收出现；然后用氨水浸泡12 h, 除去载体上吸附的助催化剂, 再用蒸馏水洗涤, 真空干燥, 以备循环使用.

本文考察了主催化剂与助催化剂配比、催化剂用量、反应温度及溶剂种类等对苯甲醇催化氧化性能的影响.

3. 结果与讨论

3.1. 制备聚合物固载氮氧自由基非均相催化剂TEMPO/CPGMA的化学过程

本文通过分子设计的构思, 将氮氧自由基固载于含有环氧基团的聚合物微球表面：首先以GMA为单体, EGDMA为交联剂, 采用悬浮聚合法制备了交联聚合物微球CPGMA, 在此微球表面含有大量环氧基团；再以4-OH-TEMPO为试剂, 在碱性条件下, 使之与微球CPGMA表面的环氧基团发生开环反应, 从而实现TEMPO的固载, 制得非均相催化剂TEMPO/CPGMA, 其制备过程如图式1所示.

3.2. 交联微球和固载氮氧自由基微球的表征

3.2.1. 红外光谱

图1为交联微球CPGMA和固载化微球TEMPO/CPGMA的FT-IR谱. 由图可见, 在交联微球CPGMA上1731 cm^{-1}处出现对应于GMA单体单元以及交联剂单体单元中酯羰基的特征吸收峰；另外906和844 cm^{-1}处的谱带为环氧键的特征吸收峰；2953 cm^{-1}处为聚合物主链亚甲基及EGDMA单体单元中亚甲基的伸缩振动吸收峰, 3000 cm^{-1}处的谱带为GMA单体单元中甲基的伸缩振动吸收峰. 由此可见, GMA与EGDMA已发生了交联共聚合反应, 得到了交联微球CPGMA.

当CPGMA固载TEMPO后, 环氧键的特征吸收峰(906和844 cm^{-1})已大为减弱, 并在1390和1160 cm^{-1}处出现了两个新峰, 分别对应于N–O键和C–O–C键的特征吸收峰, 而且于3440 cm^{-1}处出现了强烈的羟基(环氧键开

环反应的结果)伸缩振动吸收. 由此可见, 4-OH-TEMPO已与交联微球CPGMA上的环氧基团发生了开环反应, 氮氧自由TEMPO已键合在了交联微球CPGMA上, 形成了固载化微球TEMPO/CPGMA.

3.2.2. 微球的形貌

图2为交联微球CPGMA与固载化微球TEMPO/CPGMA的SEM照片. 可以看出, 交联微球CPGMA球形度良好, 粒径比较均匀; 固载TEMPO后其球形度依然保持良好, 只是表面变得有点粗糙. 这是由于微球表面发生了大分子反应(环氧基团开环反应), 将TEMPO键合在了其表面.

3.3. TEMPO固载化反应条件的优化

3.3.1. 反应物投料比

保持交联微球CPGMA的投加量为1.0 g, 同时保持溶剂的体积不变, 改变4-OH-TEMPO的投加量, 从而改变微球表面的环氧基团和4-OH-TEMPO的摩尔投料比, 进行固载化反应, 所得固载化微球TEMPO/CPGMA表面的TEMPO固载量随时间变化的曲线见图3. 可以清楚地看出, 随着摩尔投料比的增大, 即随着4-OH-TEMPO用量的增大(在溶剂体积不变的情况下, 4-OH-TEMPO浓度增加), TEMPO的固载量提高, 因而, 4-OH-TEMPO与环氧基团间的开环反应属双分子亲核取代(S_N2)反应, 增加亲核试剂4-OH-TEMPO的浓度, 使得反应速率加快, 故而固载量增大. 综合起来看, 投料比为1:2.0较适宜, 反应16 h, 可制得TEMPO固载量为3.14 mmol/g的微球TEMPO/CPGMA.

3.3.2. 溶剂极性

图4为使用DMF、1,4-二氧六环(Dioxane)、DMF+Dioxane混合液(v:v = 7:3)、DMF+Dioxane混合液(v:v = 3:7)等四种极性不同具有四种不同介电常数ε的溶剂时, 所制得的TEMPO/CPGMA表面TEMPO的固载量随反应时间的变化曲线. 由图4可见, 使用四种不同溶剂时, TEMPO固载量大小顺序为: DMF＞DMF+Dioxane (7:3)＞DMF+Dioxane (3:7)＞Dioxane, 这与它们极性大小的顺序一致, 即溶剂极性越高, TEMPO固载化反应的效果越好.

实验发现, 四种溶剂对交联微球CPGMA均有良好的溶胀性能, 即交联网络能充分伸展开来, 大分子链中的环氧基团均可以与亲核试剂保持良好的可接近性. 在此前提条件下, 溶剂对CPGMA环氧基团与4-OH-TEMPO之间的取代反应的影响主要来自溶剂的极性, 溶剂的极性越强, 溶剂与亲核试剂4-OH-TEMPO之间的偶极-偶极相互作用越强, 越有利于其分子中羟基氢质子的脱去, 有利于4-OH-TEMPO对环氧基团的亲核进攻, 促进了亲核取代反应, 即促进了TEMPO固载化反应的进行, 故本文选择DMF为反应溶剂.

3.3.3. 温度

图5给出了不同反应温度时所制微球TEMPO/CPGMA表面TEMPO固载量随时间的变化曲线. 由图可见, 温度较低时, 开环反应的效果较差, TEMPO的固载量很低; 随着温度的升高, 相同反应时间内TEMPO的固载量增加, 表明反应速度加快. 由于85 °C时TEMPO的固载量已十分接近于95 °C时, 因此在85 °C下进行固载化反应较适宜.

3.4. 非均相催化剂TEMPO/CPGMA在分子氧氧化苯甲醇过程中的催化特性

3.4.1. TEMPO/CPGMA的催化活性与催化机理

使用TEMPO固载量为3.14 mmol/g的微球TEMPO/CPGMA, 采用以下催化剂体系进行苯甲醇的氧化反应: (1) TEMPO/CPGMA+CuCl (摩尔比1:1.2); (2) TEMPO/CPGMA; (3) CuCl; (4)不加催化剂. 图6给出了4种反应体系中苯甲醛产率随反应时间的变化曲线. 可以看出, 不加催化剂的空白体系基本无反应发生; 单一加入主催化剂TEMPO/CPGMA或助催化剂CuCl的体系, 苯甲醛产率很低; 当使用TEMPO/CPGMA+CuCl共催化剂体系时, 反应20 h, 苯甲醛产率可达90%. 可见, 固载化微球TEMPO/CPGMA与CuCl构成的共催化剂体系, 对分子氧氧化苯甲醇为苯甲醛的反应具有很高的催化活性, 明显高于分子筛固载化的TEMPO+CuCl体系[26](48 h, 苯甲醛产率35%), 是实现伯醇氧化为醛的高效催化剂体系.

氮氧自由基TEMPO催化氧化醇的机理目前普遍认同的是氮羰基阳离子历程[7,10,27], 这是一非自由基反应机理. 在本催化氧化体系中, 可能的反应机理为如图式2所示: 在分子氧的氧化作用下, 助催化剂CuCl首先被氧化为高价的Cu(Ⅱ), 在其作用下, TEMPO发生单电子氧化过程, 转化为具有极强氧化性的氮羰基阳离子, 该氧化剂物种在温和的条件下, 从苯甲醇分子中提取氢, 从而将其高效地氧化为苯甲醛, 与此同时, 催化剂复原为还原态的TEMPOH, 完成催化氧化循环. 由于此反应机理中不存在自由基, 故避免了产物过度氧化为羧酸.

3.4.2. 助催化剂CuCl投料量对反应性能的影响

当固定TEMPO/CPGMA的加料量为0.90 g, CuCl的用量(表示为TEMPO与CuCl的摩尔比)不同时, 苯甲醛的产率随反应时间变化的曲线见图7. 图7显示, 随着助催

化剂CuCl用量的增加, 苯甲醛产率增高. 当TEMPO与CuCl的摩尔比为1:1.2, 反应20 h时, 苯甲醛产率约为90%, 继续增加CuCl的用量, 反应结果变化不大. 因此, 本体系TEMPO与CuCl的摩尔比为1:1.2较适宜.

3.4.3. 共催化剂体系用量对催化氧化反应的影响

图8为共催化剂体系的用量(以TEMPO/CPGMA的质量计)对苯甲醛产率的影响. 由图可见, 苯甲醛产率随共催化剂用量的增加而增高, 当催化剂用量增高至一定量(TEMPO/CPGMA的质量为0.90 g)时, 苯甲醛产率达到90%; 继续增加催化剂的用量, 苯甲醛产率的变化很微小.

3.4.4. 催化剂的循环使用性能

图9考察了固载化催化剂TEMPO/CPGMA和CuCl形成共催化体系的重复用使用性能. 可以看到, 在6次循环实验中, 第二次使用时苯甲醛产率从90%降至85%, 在其余的4次循环使用过程中, 随着循环使用次数的增加, 苯甲醛产率可基本稳定在83%以上. 同时发现, 在循环使用过程中TEMPO/CPGMA微球始终保持良好的球形度, 外观未发现明显的变化. 由此可见TEMPO/CPGMA具有良好的重复使用性能.

4. 结论

利用聚甲基丙烯酸缩水甘油酯交联微球表面的环氧基团与4-OH-TEMPO之间的开环反应, 将TEMPO固载于聚合物微球表面, 提出了一条实现TEMPO固载化的独特途径. CPGMA的环氧基团与4-OH-TEMPO之间的开环反应属S_N2亲核取代反应, 在DMF中于85 °C下进行固载化反应较为适宜. TEMPO/CPGMA与助催化剂CuCl构成共催化体系, 可在室温、常压的O_2下高效地实现苯甲醇氧化为苯甲醛, 苯甲醛选择性和产率分别为100%和90%. 适宜的反应条件为TEMPO与助催化剂CuCl摩尔比1:1.2, TEMPO/CPGMA用量0.90 g以及相应质量的CuCl. 此外, TEMPO/CPGMA催化剂具有良好的循环使用性能.