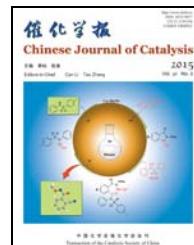


available at www.sciencedirect.comjournal homepage: www.elsevier.com/locate/chnjc**Article****TEMPO immobilized on polymer microspheres-catalyzed oxidation of cyclohexanol by molecular oxygen**

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ABSTRACT

2,2,6,6-four methyl piperidine nitroxide (TEMPO) was bonded on crosslinked poly(glycidyl methacrylate) microspheres (CPGMA microspheres) by ring opening reactions between the epoxy group on the CPGMA microspheres and the hydroxyl group of 4-OH-TEMPO. The obtained heterogeneous TEMPO-immobilized polymeric (TEMPO/CPGMA) microspheres combined with a homogeneous co-catalyst $\text{Fe}(\text{NO}_3)_3$ was used in the oxidation of cyclohexanol by molecular oxygen. The catalytic property and catalytic mechanism were examined. This combination catalyst effectively catalyzed the oxidation of cyclohexanol by molecular oxygen to cyclohexanone as the only product. Both Fe^{3+} ion and NO_3^- ion in $\text{Fe}(\text{NO}_3)_3$ together played the role of co-catalyst. For this combination catalyst, under the conditions of 1:1 molar ratio of immobilized TEMPO to $\text{Fe}(\text{NO}_3)_3$, 55 °C, ordinary pressure and with a suitable amount of this combination catalyst, the cyclohexanone yield was 44.1%, effectively transforming cyclohexanol to cyclohexanone under mild conditions.

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1. Introduction

The selective oxidation of primary and secondary alcohols to their aldehydes and ketones is an important functional group transformation in organic chemistry [1–3] which plays a very important role in both laboratory research and fine chemical production. Numerous oxidizing reagents in stoichiometric amount, such as CrO_3 , KMnO_4 and MnO_2 , have been employed to accomplish this transformation, but they generate environmentally hazardous or toxic byproducts [4–6]. From the economic and environmental viewpoints, molecular O_2 as a green oxidant has received much attention in recent years because O_2 is inexpensive and water is the only byproduct. Many catalytic systems have been developed for catalytic aerobic alcohol oxidation [7–11]. Among the various catalytic systems, the combinations of 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO) and some co-catalysts are attractive and promising [12–14]

because TEMPO is readily converted to a nitrogen carbonyl cation by a single electron oxidation, and then the nitrogen carbonyl cation as a strong oxidant enables primary and secondary alcohols to be quickly oxidized to the corresponding aldehydes or ketones with a high conversion rate and excellent selectivity. Although these homogeneous TEMPO systems exhibit high catalytic activity for aerobic alcohol oxidation, limitations still exist such as that the TEMPO chemical agent is expensive, and as a homogeneous catalyst it is difficult to recover and recycle after the reaction. It is possible to overcome these limitations by immobilizing the TEMPO catalyst on a solid support, and the heterogeneous TEMPO catalyst would have the advantages of easy separation and efficient recycling [15–17].

TEMPO has been immobilized on various solid supports, including silica gel, molecular sieves, and polymeric resins [18–20]. Among these supports, the polymer resin is advantageous because active groups can be easily introduced onto it by

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chemical modification, and these active groups can facilitate the chemical bonding of TEMPO on the polymer resin. The literature rarely has studied about heterogeneous TEMPO catalysts supported on polymer resins. In our previous study, cross-linked poly(glycidyl methacrylate) microspheres (CPGMA microspheres) were prepared by suspension polymerization, and TEMPO was bonded to the CPGMA microspheres by ring opening reactions between the epoxy groups on the CPGMA microspheres and the hydroxyl groups of 4-OH-TEMPO, resulting in the heterogeneous catalyst microspheres TEMPO/CPGMA [21]. In the present work, the heterogeneous catalyst TEMPO/CPGMA was combined with a co-catalyst $\text{Fe}(\text{NO}_3)_3$ and was used in the aerobic oxidation of cyclohexanol as a secondary alcohol under mild conditions. The catalyst system constituted by the heterogeneous TEMPO/CPGMA and homogeneous $\text{Fe}(\text{NO}_3)_3$ effectively catalyzed the aerobic oxidation of cyclohexanol to cyclohexanone as the sole product with good activity. It was also found that both the Fe^{3+} and NO_3^- species in $\text{Fe}(\text{NO}_3)_3$ showed work together. Although there have been some reports on the aerobic oxidation of secondary alcohols by a homogeneous TEMPO analog combined with $\text{Fe}(\text{NO}_3)_3$ [22,23], we report for the first time that the heterogeneous TEMPO, i.e. TEMPO immobilized on polymer microspheres, combined with $\text{Fe}(\text{NO}_3)_3$ can be used for the aerobic oxidation of a secondary alcohol. The catalytic oxidation mechanism was proposed. The result is valuable for the green and effective oxidation transformation of secondary alcohols in organic synthesis.

2. Experimental

2.1. Materials and instruments

Glycidyl methacrylate (GMA) was purchased from Nanhang Chemical Ltd. (Suzhou, China) and purified by distillation under vacuum before use. Ethylene dimethacrylate (EGDMA) was supplied by Yantai Kaihua Chemical Co., Ltd. (Shandong, China) and purified by distillation under vacuum before use. 4-Hydroxy-2,2,6,6-four methyl piperidine nitroxide (4-OH-TEMPO) was supplied by Ruishuo Chemical Co., Ltd. (Shanghai, China). Cyclohexanol was supplied by Beijing Chemical Reagent Company (China). Other chemicals were analytically pure reagents purchased from Chinese companies.

The instruments used in this study were: Perkin-Elmer 1700 infrared spectrometer (FTIR, Perkin-Elmer Company, USA); 438vp scanning electron microscopy (SEM, LEO company, UK); GC-920 gas chromatograph (GC, Shanghai Haixin Chromatograph Co., Ltd.)

2.2. Preparation and characterization of the heterogeneous catalyst TEMPO/CPGMA

Using the procedure described in Ref. [21] (with some changes), the heterogeneous catalyst TEMPO/CPGMA was prepared. (1) The crosslinked polymeric microspheres CPGMA were first prepared by suspension polymerization. The continuous phase was comprised by distilled water containing

polyvinyl alcohol and NaCl. The monomer GMA was mixed with the crosslinker EGDMA as the oil phase, and this mixture was used as the dispersed phase. By adjusting the agitation speed to ensure good mixing of the two phases, a suspension polymerization system was formed. The initiator azoisobutyronitrile (AIBN) was then added, and the crosslinking copolymerization of GMA and EGDMA was carried out at 55 °C for 5 h under N_2 atmosphere, obtaining translucent crosslinked polymeric microspheres GMA/EGDMA (denoted by CPGMA microspheres because GMA was the main monomer). The average diameter of CPGMA microspheres was 100 μm measured by an optical microscope. (2) TEMPO was bonded onto CPGMA microspheres by a polymer reaction. CPGMA microspheres were first soaked and swelled in *N,N*-dimethylformamide (DMF), and then 4-OH-TEMPO was added into the mixture. The ring opening reaction between the epoxy groups on the CPGMA microspheres and the hydroxyl groups of 4-OH-TEMPO was conducted at 85 °C for 12 h under N_2 atmosphere with Na_2CO_3 as a catalyst. The TEMPO-immobilized microsphere TEMPO/CPGMA catalyst was obtained. The TEMPO/CPGMA microspheres were characterized by FTIR, SEM and a chemical analysis method [21]. The immobilized amount of TEMPO on the TEMPO/CPGMA microspheres was 3.14 mmol/g.

2.3. Catalytic oxidation of cyclohexanol with molecular O_2

TEMPO/CPGMA microspheres in combination with $\text{Fe}(\text{NO}_3)_3$ was used in the catalytic oxidation of cyclohexanol with molecular O_2 as oxidant at normal pressure. A typical procedure is as follows. In a reactor equipped with a mechanical stirrer, reflux condenser, thermometer and O_2 inlet, 50 mL of glacial acetic acid and 10 mL of cyclohexanol were added, followed by adding the combination catalysts containing 1.10 g of TEMPO/CPGMA microspheres and 0.242 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the co-catalyst. Oxygen at normal pressure was introduced into the mixture (15 mL/min). The oxidation reaction was performed at 55 °C with continuously stirring for 36 h. Samples of the reaction mixture were taken at fixed time intervals, and then measured immediately by a gas chromatograph (GC) with the internal standard method. The GC analysis results showed that cyclohexanone was the only product, and so the cyclohexanone yield was the conversion of cyclohexanol. The cyclohexanone yield was calculated from the GC data. After the oxidation reaction, the TEMPO/CPGMA microspheres were soaked, washed with acetic acid and ethanol in turn to completely remove cyclohexanone physically attached on the microspheres, and dried under vacuum. The recovered TEMPO/CPGMA microspheres were reused in the oxidation reaction of cyclohexanol under the same conditions to examine their recycling performance.

2.4. Examining the main factors in the catalytic oxidation of cyclohexanol

In order to understand the catalytic mechanism of cyclohexanol oxidation by molecular oxygen, the catalytic property of the combination catalyst, TEMPO/CPGMA microspheres and

$\text{FeCl}_3+\text{NaNO}_3$ was investigated. The effects of ratio of TEMPO/CPGMA to $\text{Fe}(\text{NO}_3)_3$, combination catalyst amount and reaction temperature were examined.

3. Results and discussion

3.1. Preparing the TEMPO/CPGMA microspheres and their chemical structure

In this work, the nitroxide free radical was immobilized on the surface of the polymer microspheres containing epoxy groups by an elaborate molecular design. CPGMA microspheres were first prepared by suspension copolymerization of GMA and EGDMA used as a crosslinker. There were abundant active groups, namely, the epoxy groups, on the CPGMA microspheres. Through the ring opening reaction between the epoxy group on the CPGMA microspheres and hydroxyl group of 4-OH-TEMPO under alkaline condition, TEMPO was chemically immobilized on the surface of the CPGMA microspheres, and TEMPO/CPGMA microspheres were prepared. The process to prepare TEMPO/CPGMA microspheres and their chemical structures is schematically depicted in Scheme 1. In the characterization of the TEMPO/CPGMA microspheres, the infrared spectrum confirmed their chemical structure, and their morphology was observed by SEM. The detailed results are given in Ref. [21].

3.2. Catalytic activity and mechanism

The oxidation of cyclohexanol by molecular oxygen was catalyzed by the TEMPO/CPGMA microspheres and $\text{Fe}(\text{NO}_3)_3$ combination catalysts, and was carried out under normal

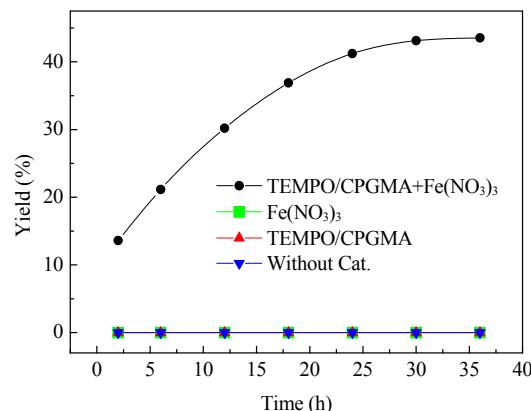
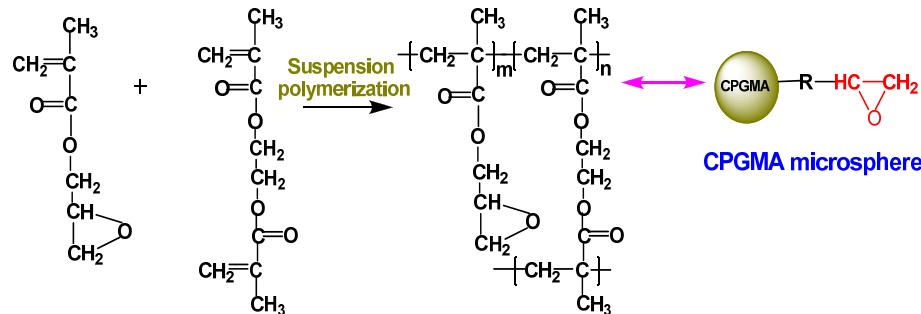


Fig. 1. Curves of cyclohexanone yield with time using the combination of TEMPO/CPGMA and $\text{Fe}(\text{NO}_3)_3$ as co-catalyst or the single components as catalyst. Reaction conditions: 55 °C, O_2 ordinary pressure, acetic acid as solvent.

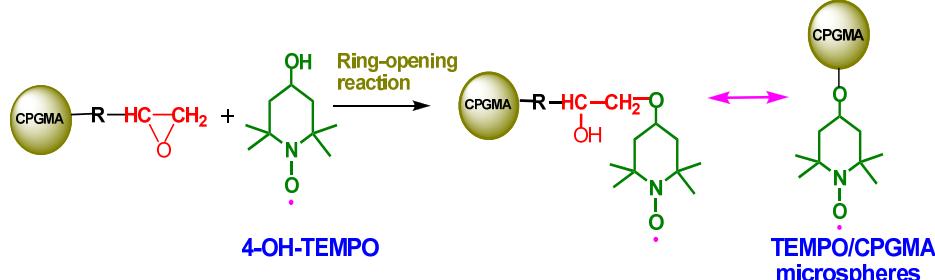
pressure of molecular oxygen. Fig.1 gives the curve of cyclohexanone yield, i.e., conversion of cyclohexanol versus time. For comparison, the oxidation reaction was also conducted in the presence of TEMPO/CPGMA alone, $\text{Fe}(\text{NO}_3)_3$ alone and with no catalyst, and it was found that there was no reaction in the three systems.

For the reaction system with TEMPO/CPGMA microspheres and $\text{Fe}(\text{NO}_3)_3$ added, the oxidation of cyclohexanol was obvious, and the cyclohexanone yield was 44% in 36 h. This showed the immobilized TEMPO in combination with $\text{Fe}(\text{NO}_3)_3$ effectively catalyzed the oxidation of cyclohexanol by molecular oxygen. The results showed only their combination had a catalytic role in the oxidation of cyclohexanol by molecular oxygen.

(1) Preparation of crosslinked polymer microspheres CPGMA by suspension polymerization



(2) Immobilization of TEMPO on CPGMA microspheres via ring-opening reaction of epoxy group



Scheme 1. Chemical structure of CPGMA and TEMPO/CPGMA microspheres.

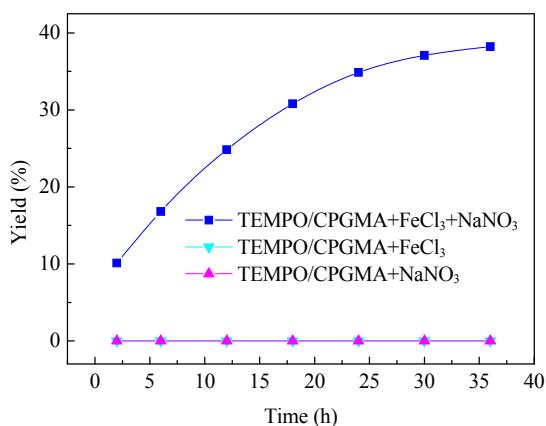
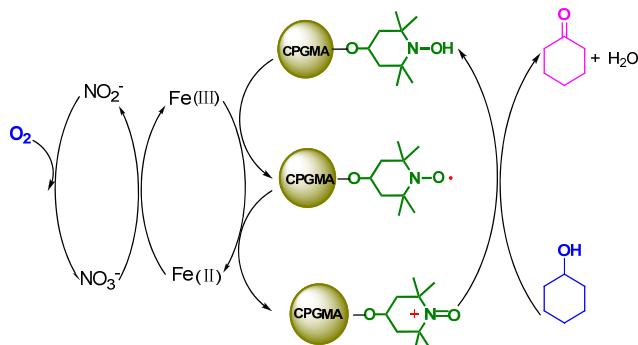


Fig. 2. Curves of cyclohexanone yield with time using combination of TEMPO/CPGMA, FeCl₃ and NaNO₃ as catalyst as well as using other component combination as catalyst. Reaction conditions: 55 °C, O₂ ordinary pressure, acetic acid as solvent.

As reviewed above, various combinations of TEMPO or immobilized TEMPO and a co-catalyst can catalyze the aerobic oxidation of alcohols. In the present catalyst system, the immobilized TEMPO was the main catalyst, and Fe(NO₃)₃ was a co-catalyst. In order to confirm that Fe³⁺ and NO₃⁻ in Fe(NO₃)₃ should work together, a combination of TEMPO/CPGMA, FeCl₃ and NaNO₃ (with a molar ratio of FeCl₃ to NaNO₃ of 1:3) was used in the reaction. At the same time, the combination of TEMPO/CPGMA and FeCl₃ or NaNO₃ were also used, and the results are given in Fig. 2.

When TEMPO/CPGMA, FeCl₃ and NaNO₃ was used as catalyst, the cyclohexanone yield reached nearly 40% in 36 h, close to that of TEMPO/CPGMA and Fe(NO₃)₃, suggesting that the combination of FeCl₃ and NaNO₃ can take place of Fe(NO₃)₃ in the catalytic system. However, no oxidation reaction was observed when using the combination of TEMPO/CPGMA and FeCl₃ or NaNO₃. The results demonstrated that only Fe³⁺ or NO₃⁻ did not play a co-catalyst role in the catalytic system, and only their combination did. The above results confirmed that in the combination of TEMPO/CPGMA microspheres and Fe(NO₃)₃, both of Fe³⁺ ion and NO₃⁻ ion must act together. From the above experiments and by referring to published TEMPO catalytic systems [24,25], a catalytic oxidation mechanism is proposed in Scheme 2.



Scheme 2. Catalytic oxidation mechanism of the combination of TEMPO/CPGMA and Fe(NO₃)₃.

The immobilized TEMPO is responsible for the main oxidation reaction of cyclohexanol with the help of Fe(III) that initiates a series of electron and proton transfer. During the redox processes, the immobilized TEMPO is oxidized to oxo-ammonium ion by Fe(III) [22]. The oxo-ammonium ion that is a well-known highly efficient oxidant oxidizes cyclohexanol to cyclohexanone and release the immobilized TEMPOH, while Fe(III) is reduced to Fe(II) finally. The role of NO₃⁻ is for the oxidation of Fe(II) to Fe(III), and at the same time, NO₃⁻ is reduced to NO₂⁻ that was again oxidized to NO₃⁻ by dissolved oxygen. There are three cycles in the redox processes as presented in Scheme 2. With repeating of the three cycles, cyclohexanol is continuously transformed into cyclohexanone.

3.3. Main factors in the catalytic oxidation of cyclohexanol

3.3.1. Effect of molar ratio of immobilized TEMPO to Fe(NO₃)₃

In the reaction system, TEMPO/CPGMA microspheres in a specific amount (1 g) were added, and the added amount of the co-catalyst Fe(NO₃)₃·9H₂O was varied. Fig. 3 gives the results of the oxidation of cyclohexanol.

With increasing amount of Fe(NO₃)₃, the cyclohexanone yield in the same period of time increased. When the molar ratio of the immobilized TEMPO to Fe(NO₃)₃ is equal to 1:1, the cyclohexanone yield reached 38% in 36 h, and adding more Fe(NO₃)₃ did not improve the reaction significantly. Therefore, 1:1 molar ratio of TEMPO to Fe(NO₃)₃ was considered to be optimum.

3.3.2. Effect of combination catalyst amount

The combination of TEMPO/CPGMA and Fe(NO₃)₃ in the molar ratio of 1:1 was added into the oxidation system. With the fixing of the other reaction conditions, the combination catalyst amount was varied and the results of the oxidation of cyclohexanol are given in Fig. 4.

Fig. 4 displays that the cyclohexanone yield in the same period of time increased with increasing the amount of combination catalyst. However, after the catalyst amount was increased to 1.1 g the cyclohexanone yield was 44.1% in 36 h, further

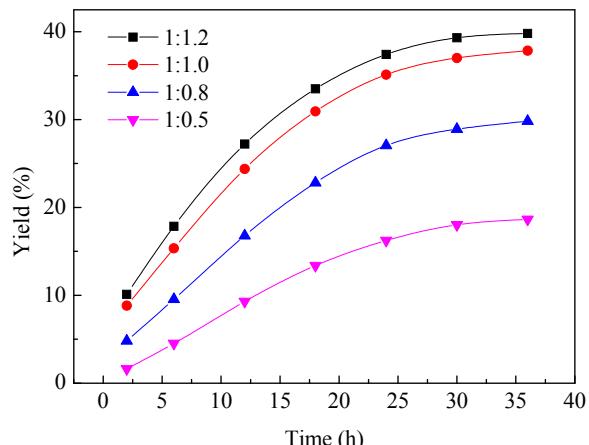


Fig. 3. Curves of cyclohexanone yield with time using different molar ratios of immobilized TEMPO to Fe(NO₃)₃. Reaction conditions: 55 °C, O₂ ordinary pressure, acetic acid as solvent.

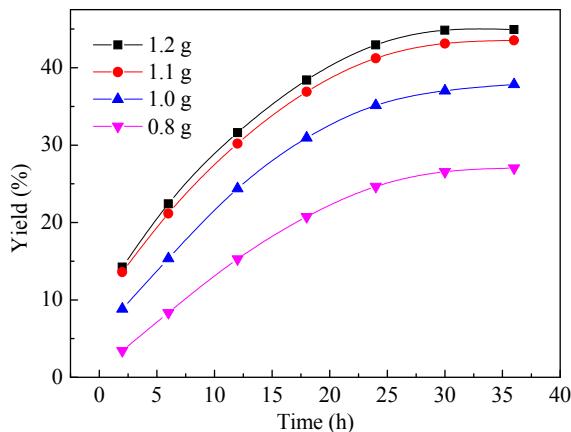


Fig. 4. Curves of cyclohexanone yield with time with different amounts of combination catalyst of TEMPO/CPGMA and $\text{Fe}(\text{NO}_3)_3$. Reaction conditions: 55 °C, O_2 ordinary pressure, acetic acid as solvent, ratio of TEMPO to $\text{Fe}(\text{NO}_3)_3$ 1:1.

increasing the combination catalyst amount no longer affected the reaction significantly. Therefore, 1.1 g of this combination catalyst was optimum.

3.3.3. Effect of temperature

By fixing the other reaction conditions and changing the reaction temperature, the oxidation of cyclohexanol by molecular oxygen was performed as shown in Fig. 5.

It can be seen that cyclohexanone yield increased with temperature. However, after the temperature had increased to 55 °C, the variation of the reaction rate with temperature became insignificant. Therefore, the suitable reaction temperature should be 55 °C.

3.4. Reuse property of the catalyst

The recycle and reuse experiments for the combination catalyst, TEMPO/CPGMA and $\text{Fe}(\text{NO}_3)_3$ with a molar ratio of 1:1, were conducted to examine its stability (only the recycle and reuse property of the TEMPO/CPGMA microspheres was tested

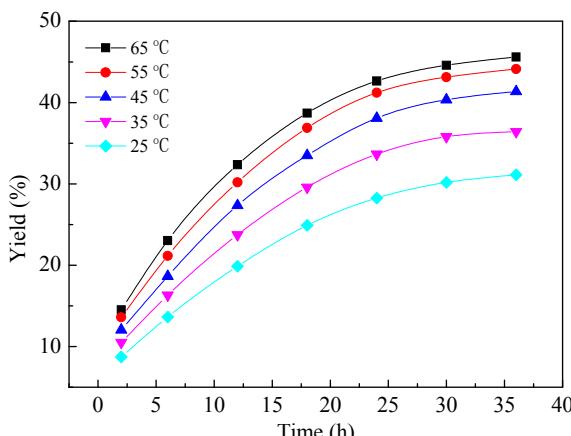


Fig. 5. Curves of cyclohexanone yield with time at different temperatures. Reaction conditions: O_2 ordinary pressure, acetic acid as solvent, ratio of TEMPO to $\text{Fe}(\text{NO}_3)_3$ 1:1, combination catalyst 1.1 g.

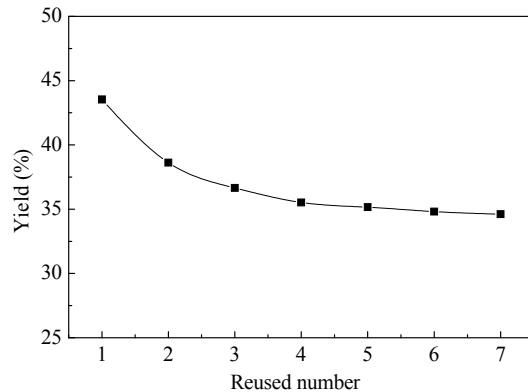


Fig. 6. Effect of cycle number on catalyst activity. Reaction conditions: 55 °C, O_2 ordinary pressure, glacial acetic acid as solvent, 36 h.

because $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as a homogeneous catalyst was added in each test). Fig. 6 shows the cyclohexanone yield in 36 h as a function of the number of cycles for this combination catalyst system.

It can be observed that during the consecutive reuse of 7 times, the combination catalyst was stable to some extent. In the second use, the cyclohexanone yield decreased obviously from 44.1% to 38.6%. In the third use, the cyclohexanone yield decreased from 38.6% to 36.5%. Thereafter, the combination catalyst was stable, and the cyclohexanone yield remained at 35%.

4. Conclusions

TEMPO was bonded onto polymeric CPGMA microspheres by a polymer reaction to give TEMPO-immobilized microspheres, TEMPO/CPGMA microspheres. These microspheres in combination with $\text{Fe}(\text{NO}_3)_3$ were used in the oxidation of cyclohexanol by molecular oxygen. The catalytic property of this combination catalyst, TEMPO/CPGMA and $\text{Fe}(\text{NO}_3)_3$, was investigated, and the catalytic mechanism was inferred. This combination catalyst has good catalytic activity in the oxidation of cyclohexanol by molecular oxygen. Under the optimized conditions, with a molar ratio of the immobilized TEMPO to $\text{Fe}(\text{NO}_3)_3$ of 1:1, 55 °C, standard pressure of oxygen and with an appropriate amount of this combination catalyst, the cyclohexanone yield was 44.1%. This combination catalyst gave only cyclohexanone, showing excellent catalytic selectivity. In the catalytic oxidation, the immobilized TEMPO was the catalyst responsible for the oxidation of cyclohexanol, while $\text{Fe}(\text{NO}_3)_3$ as co-catalyst helped the TEMPO/CPGMA microspheres complete the redox cycle. Both Fe^{3+} and NO_3^- in $\text{Fe}(\text{NO}_3)_3$ together play the co-catalyst role.

References

- [1] Hu Z Z, Kerton F M. *Appl Catal A*, 2012, 413-414: 332
- [2] Zhu C, Ji L, Wei Y Y. *Catal Commun*, 2010, 11: 1017
- [3] Qian W X, Jin E L, Bao W L, Zhang Y M. *Tetrahedron*, 2006, 62: 556
- [4] Ahmad J U, Figiel P J, Räisänen M T, Leskelä M, Repo T. *Appl Catal A*, 2009, 371: 17

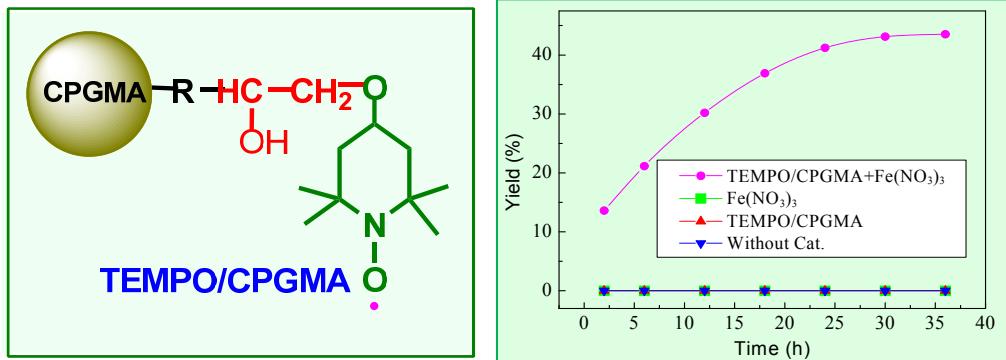
Graphical Abstract

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TEMPO immobilized on polymer microspheres-catalyzed oxidation of cyclohexanol by molecular oxygen

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North University of China



TEMPO-immobilized polymeric microspheres, TEMPO/CPGMA microspheres, were prepared. A combination of the TEMPO/CPGMA microspheres as heterogenous catalyst and Fe(NO₃)₃ as homogenous co-catalyst was used in the oxidation of cyclohexanol by molecular oxygen. This combination catalyst effectively catalyzed the oxidation of cyclohexanol by molecular oxygen and cyclohexanol was transformed into cyclohexanone as the sole product.

- [5] Liu L, Ji L Y, Wei Y Y. *Catal Commun*, 2008, 9: 1379
- [6] Yoshida A, Takahashi Y, Ikeda T, Azemoto K, Naito S. *Catal Today*, 2011, 164: 332
- [7] Wang F, Ueda W. *Appl Catal A*, 2008, 346: 155
- [8] Shen H Y, Zhou SC, Wei M H, Zong H X. *React Funct Polym*, 2006, 66: 827
- [9] Figiel P J, Sobczak J M. *J Mol Catal*, 2009, 263: 167
- [10] Ramakrishna D, Bhat B R. *Inorg Chem Commun*, 2011, 14: 155
- [11] He J L, Wu T B, Jiang T, Zhou X S, Hu B J, Han B X. *Catal Commun*, 2008, 9: 2239
- [12] Liaigre B, Belgisir E M. *Electrochim Commun*, 2005, 7: 312
- [13] Mei Z W, Omote T, Mansour M, Kawafuchi H, Takaguchi Y, Jutand A, Tsuboi S, Inokuchi T. *Tetrahedron*, 2008, 64: 10761
- [14] Wang Q F, Zhang Y, Zheng G X, Tian Z Z, Yang G Y. *Catal Commun*, 2011, 14: 92
- [15] Benaglia M, Puglisi A, Holcknecht O, Quici S, Pozzi G. *Tetrahedron*, 2005, 61: 12058
- [16] Tanyeli C, Gümüs A. *Tetrahedron Lett*, 2003, 44: 1639
- [17] Wang L Y, Li J, Zhao X P, Lü Y, Zhang HY, Gao S. *Tetrahedron*, 2013, 69: 6041
- [18] Testa M L, Ciriminna R, Hajji C, Garcia E Z, Ciclosi M, Arques J S, Pagliaro M. *Adv Synth Catal*, 2004, 346: 655
- [19] Liu L, Ma J J, Ji L Y, Wei Y Y. *J Mol Catal A*, 2008, 291: 1
- [20] Gilhespy M, Lok M, Baucherel X. *Catal Today*, 2006, 117: 114
- [21] Yu Y L, Gao B J, Li Y F. *Chin J Catal* (余依玲, 高保娇, 李艳飞. 催化学报), 2013, 34: 1776
- [22] Wang X L, Liang X M. *Chin J Catal* (王心亮, 梁鑫森. 催化学报), 2008, 29: 935
- [23] Liu J X, Ma S M. *Tetrahedron*, 2013, 69: 10161
- [24] Yang G Y, Guo Y C, Wu G H, Zheng L W, Song M P. *Progr Chem* (杨贵羽, 郭彦春, 武光辉, 郑立稳, 宋毛平. 化学进展), 2007, 19: 1727
- [25] Rossi L I, Martín S E. *Appl Catal A*, 2003, 250: 271

聚合物微球固载的催化剂TEMPO在分子氧氧化环己醇过程中的催化特性

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摘要: 醇氧化为羧基化合物是有机合成工业中最重要的化学转变之一, 在实验室研究和精细化工生产中都占有非常重要的地位。使用传统的化学计量强氧化剂(如CrO₃, KMnO₄, MnO₂等), 不但成本高及反应条件苛刻, 还会产生大量污染环境的废弃物。因此, 需要大力开展高效、绿色化的醇转变为羧基化合物的氧化途径。以2,2,6,6-四甲基哌啶氮氧自由基(TEMPO)为催化剂, 分子氧为氧化剂, 可在温和条件下绿色化地实现醇的氧化转变。该催化氧化作用的实质是TEMPO经过单电子氧化过程转化为相应的氮羧基阳离子, 该阳离子是一个具有强氧化性的氧化剂, 可将伯醇和仲醇分别快速地、高转化率、高选择性地氧化为对应的醛或酮。然而, 目前使用的TEMPO大多为均相催化剂, 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, 严重制约着这一催化体系的发展。本文将TEMPO化学键合在聚合物载体上, 在非均相催化剂的作用下, 以期实现环己醇的分子氧氧化, 将其转变为环己酮。首先采用悬浮聚合法, 制备了交联聚甲基丙烯酸缩水甘油酯(CPGMA)微球, 该聚合物微球表面含有大量环氧基团, 为实现TEMPO的固载化提供了条件。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, 从而将TEMPO键合于微球表面, 制得了固载有TEMPO的聚合物微球TEMPO/CPGMA。将此非均

相催化剂与 $\text{Fe}(\text{NO}_3)_3$ 组成共催化体系, 应用于分子氧氧化环己醇的催化氧化过程, 深入考察了该共催化体系的催化性能, 并探索研究了催化氧化机理, 考察了主要条件对催化氧化反应的影响。结果表明, 共催化体系TEMPO/CPGMA+ $\text{Fe}(\text{NO}_3)_3$ 可以有效地催化分子氧氧化环己醇的氧化过程, 将环己醇转化为唯一的产物环己酮, 显示出良好的催化选择性。助催化剂 $\text{Fe}(\text{NO}_3)_3$ 化学结构中的 Fe^{3+} 离子和 NO_3^- 离子两种物种均参与催化过程, 共同发挥助催化剂的作用, 伴随着两种价态铁物种 $\text{Fe}(\text{II})$ 与 $\text{Fe}(\text{III})$ 的转变以及 NO_3^- 与 NO_2^- 之间的转变, 固载化的氮氧自由基TEMPO不断地转变为氮簇基阳离子, 该氧化剂物种使环己醇的氧化反应不断地循环进行。对于共催化体系TEMPO/CPGMA+ $\text{Fe}(\text{NO}_3)_3$ 的使用, 适宜的反应条件为TEMPO与 $\text{Fe}(\text{NO}_3)_3$ 的摩尔比为1:1, 55 °C, 通入常压 O_2 。反应35 h, 环己酮的转化率可达到44.1%。因此, 在温和条件下, 使用固载化的TEMPO, 有效地实现了环己醇向环己酮的转化。此外, 固载化催化剂TEMPO/CPGMA在循环使用过程中表现出良好的重复使用性能。

关键词: 氮氧自由基; 聚甲基丙烯酸缩水甘油酯; 固载化; 组合催化剂; 环己醇氧化; 分子氧

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