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Article

Enhanced phenol hydroxylation with oxygen using a ceramic membrane distributor

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ABSTRACT

A CuO/TiO₂ catalyst was prepared by impregnation and characterized by X-ray diffraction, transmission electron microscopy, and temperature-programmed reduction. Two types of dispersed species formed on the TiO₂ surface, which were possibly isolated and polymeric CuO species. The CuO catalyst interacted strongly with the TiO₂ support. A porous ceramic membrane was used as a distributor to control the supply of oxygen in phenol hydroxylation over the CuO/TiO₂ catalyst. Compared to a direct feed of oxygen without a membrane, the yield of dihydroxybenzene (DHB) increased by 13% using a porous ceramic membrane with a pore size of 0.5 μm as an oxygen distributor. This is because the membrane distributor produced numerous small oxygen bubbles, increasing the volumetric oxygen transfer coefficient and gas-liquid mass transfer. Optimizing reaction conditions resulted in a yield of DHB of 2.5%. Scanning electron microscope observation of the used ceramic membrane showed that it possessed excellent thermal and chemical stability.

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1. Introduction

Dihydroxybenzene (DHB) compounds including hydroquinone and catechol are important chemical intermediates [1]. Phenol hydroxylation is a green route to synthesize DHB that has attracted considerable attention. The main oxidants used in phenol hydroxylation include hydrogen peroxide [2,3] and oxygen [4]. Oxygen is an excellent oxidizing agent because it is inexpensive, environmentally benign, and resists further oxidation.

Phenol hydroxylation using oxygen is limited by the activation of oxygen and mass transfer. One way to improve mass transfer is to use porous ceramic membranes that contain numerous micro- or nanosized pores as distributors. Such membranes control the supply of oxygen by forcing it to form many small bubbles, which increases gas-liquid mass transfer and thus promotes the reaction. Membrane distributors have been

investigated extensively. Coronas et al. [5] used ceramic membranes as oxygen distributors in the oxidative coupling of methane. The selectivity using ceramic membranes was significantly higher than that using a fixed-bed reactor. We have used a ceramic membrane as a reactant distributor to control the supply of H₂O₂ in phenol hydroxylation over titanium silicalite catalyst [6], improving the selectivity for DHB. However, using a ceramic membrane as a distributor to control the supply of oxygen in phenol hydroxylation has not been reported.

In the present work, we use a porous ceramic membrane as a distributor to control the supply of oxygen in phenol hydroxylation over a CuO/TiO₂ catalyst in an attempt to enhance gas-liquid mass transfer and increase the yield of DHB. The CuO/TiO₂ catalyst was prepared by impregnation and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and temperature-programmed reduction (TPR). The sulphate method was used to measure the volumet-

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ric oxygen transfer coefficient of the system. The effect of the membrane distributor on the yield of DHB was investigated, and the reaction conditions were optimized.

2. Experimental

2.1. Preparation and characterization of catalyst

Copper catalysts are used in a wide range of organic syntheses, especially in liquid phase oxidation of aromatic compounds [7–10]. Highly dispersed copper species are considered the active sites in phenol hydroxylation [10]. Here, a CuO/TiO₂ catalyst was prepared by impregnation for use in phenol hydroxylation with oxygen. Cu(NO₃)₂·3H₂O (AR, Shanghai Sinpeuo Fine Chemical Co., Ltd., China) and anatase TiO₂ (Qingdao Panzhihua Titanium Company, China) were added to deionized water (50 ml). The solution was magnetically stirred for 8 h and then evaporated under reduced pressure. The residue was dried at 373 K overnight and calcined at 673 K in air for 5 h. The CuO loading was 7 wt%.

XRD was carried out on a diffractometer (Bruker D8 Advance, Germany) using Cu K α radiation at 40 kV and 30 mA with a scanning rate of 0.2°/s. TPR was conducted using an analyzer (BELCAT-A, BEL, Japan). Prior to reduction, the sample was pretreated in an Ar stream at 573 K for 2 h and then cooled to 323 K. The sample was then exposed to an H₂/Ar mixture (10% H₂ by volume) and the temperature was raised to 1023 K at a rate of 10 K/min. The consumption of H₂ in the reactant stream was detected by a thermal conductivity cell. The catalyst morphology was examined by TEM (JEM-2011, JEOL, Japan) operating at 200 kV. Samples were prepared for TEM observation by sonication in ethanol for 10 min and subsequent deposition onto carbon-coated copper grids.

2.2. Phenol hydroxylation

Phenol hydroxylation with oxygen was carried out in the system depicted in Fig. 1, which consisted of a slurry reactor, membrane module, heating system, and oxygen cylinder. The slurry reactor was made of glass and possessed a working volume of 250 ml. Ceramic membranes with an outer diameter of 12 mm, inner diameter of 8 mm, and length of 6 cm were provided by Jiangsu Jiuwu Hi-Tech Co., Ltd., China. One end of the membrane tube was sealed by glazing, and the other end was connected to the oxygen cylinder. During the reaction, the oxygen flowed into the membrane tube, and then passed through the membrane pores into the reaction solution to participate in the reaction. The oxygen flow was controlled by a pneumatic rotameter.

Ascorbic acid (AR grade, Shanghai Sinopharm Chemical Reagent Co., Ltd., China), CuO/TiO₂ catalyst, phenol (20 ml, AR grade, Shanghai Sinopharm Chemical Reagent Co., Ltd., China), and aqueous acetic acid (200 ml, AR grade, Shanghai Shenbo Chemical Co., Ltd., China) were added to the reactor. The stirred mixture was heated to 308 K. Oxygen was then flowed into the reactor to start the phenol hydroxylation.

The products were analyzed by a high-performance liquid

Fig. 1. Experimental setup for phenol hydroxylation using oxygen as the oxidizing agent. 1: condenser pipe; 2: reactor; 3: membrane module; 4: membrane; 5: rotator; 6: thermometer; 7: water bath; 8: pneumatic rotameter.

chromatograph (HPLC, Agilent 1200 Series, USA) equipped with a diode array detector and an auto-sampler. Chromatographic separations were performed at 303 K using a column (ZORBAX Eclipse XDB-C18, 4.6 mm × 250 mm). A mobile phase composed of 40% methanol and 60% water at a flow rate of 1 ml/min was used. A wavelength of 277 nm was used to monitor the separation and the injection volume was 5 μ l.

The morphology of the membranes was examined using a field emission scanning electron microscope (FESEM, Hitachi S-4800, Hitachi, Japan).

3. Results and discussion

3.1. Characterization of catalyst

3.1.1. XRD results

XRD patterns of the CuO/TiO₂ catalyst and TiO₂ are presented in Fig. 2. Compared with the XRD pattern of TiO₂, two obvious peaks at $2\theta = 35.5^\circ$ and 39.0° were observed in that of the catalyst, corresponding to the (-111) and (111) crystal faces of monoclinic CuO. The intensity of these CuO peaks was weak, possibly because of the small particle size or low crystallinity of CuO.

Fig. 2. XRD patterns of the CuO/TiO₂ catalyst and TiO₂.

Fig. 3. TEM and HRTEM images of the CuO/TiO₂ catalyst. (a) TEM image of CuO/TiO₂; (b) HRTEM image of CuO/TiO₂. Inset: Fourier reconstruction of the area indicated by a rectangle.

3.1.2. TEM results

TEM and HRTEM images of the CuO/TiO₂ catalyst are shown in Fig. 3. CuO particles with a size of about 3 nm were well dispersed on the surface of the TiO₂ support. The lattice spacing of 0.186 nm was consistent with the (-202) crystal face of CuO.

3.1.3. TPR results

TPR characterization of the CuO/TiO₂ catalyst (Fig. 4) revealed that it exhibited three separate reduction peaks centered at 443, 541, and 610 K, and the areas of the peaks at 541 and 610 K were obviously larger than that at 443 K. Lasson et al. [11] attributed the peak at 443 K to the reduction of isolated CuO species, and those in the region of 503–553 K to the reduction of polymeric species. The peak at 610 K also might be related to the reduction of polymeric species interacting more strongly with the TiO₂ support than those corresponding to the peak at 541 K. These results indicate that there are both isolated and polymeric CuO species on the TiO₂ surface, with a larger proportion of polymeric CuO species than isolated ones.

3.2. Effect of membrane distributor on phenol hydroxylation

The volumetric oxygen transfer coefficient was measured by the sulphate method [12] as a performance index for oxygen transfer. As shown in Table 1, when an alumina membrane with a pore size of 0.5 μm or a mullite membrane with a pore

Fig. 4. TPR profile of the CuO/TiO₂ catalyst.

Table 1

Effect of membrane distributor on the volumetric oxygen transfer coefficient.

Feeding mode	Pore size or diameter (μm)	$k_L a^a$ (h ⁻¹)
Alumina membrane	0.5	1183
Mullite membrane	1	1173
PU tube	4400	145

^a Volumetric oxygen transfer coefficient.

size of 1 μm was used as a distributor to control the supply of oxygen in phenol hydroxylation, the volumetric oxygen transfer coefficient was about eight times higher than that in direct feeding mode when a PU tube was used to supply oxygen. This is because the membrane distributor created many small oxygen bubbles, which increased the gas-liquid mass transfer area and enhanced the mass transfer capacity of oxygen.

Alumina and mullite membranes with pore sizes of 0.5 and 1 μm, respectively, were used as distributors to control the supply of oxygen in phenol hydroxylation. The direct feeding mode was also used for comparison. As presented in Fig. 5, the yield of DHB increased when a ceramic membrane distributor was used. The ceramic membrane distributor with a pore size of 0.5 μm increased the yield of DHB by 13%. In addition, the stirring rate had an obvious effect on the yield of DHB, as shown in Fig. 6. The yield of DHB increased as the stirring rate was increased in the experimental range. Therefore, the reaction process was diffusion controlled. Combining these results with those in Table 1 revealed that introducing a membrane distributor into the reactor increased both the volumetric oxygen transfer coefficient and mass transfer capacity of oxygen. Therefore, the observed increase of the yield of DHB should be caused by the enhanced gas-liquid mass transfer related to the introduction of a membrane distributor. Figure 5 also shows that the yield of DHB first increased and then remained constant after a certain period, which should be related to the type of phenol conversion and selectivity for DHB changing. The conversion of phenol generally increased over time, whereas the selectivity for DHB decreased (data not shown here). The decrease of selectivity for DHB was caused by the further oxidation of DHB to benzoquinone and other by-products [6]. In-

Fig. 5. Effect of membrane distributor on the yield of DHB. Reaction conditions: stirring rate 470 r/min, oxygen flow 100 ml/min, catalyst concentration 48.8 g/L, ascorbic acid concentration 50 g/L, acetic acid concentration 80%.

Fig. 6. Effect of stirring rate on the yield of DHB. Reaction conditions: oxygen flow 100 ml/min, catalyst concentration 43.8 g/L, ascorbic acid concentration 40 g/L, acetic acid concentration 60%.

Introducing a membrane distributor caused a smaller increase in the yield of DHB than that of volumetric oxygen transfer coefficient. This indicates that the reaction process was also affected by other factors such as stirring rate and oxygen flow. A membrane distributor with smaller pore size promoted the synthesis of DHB more than one with larger pores. However, the required operation pressure obviously increases with decreasing membrane pore size. As a result, an alumina membrane with a pore size of 0.5 μm was chosen as the oxygen distributor in phenol hydroxylation.

3.3. Optimization of operating conditions

3.3.1. Effect of stirring rate

Figure 6 shows the effect of stirring rate on phenol hydroxylation. The yield of DHB increased with stirring rate because an increased stirring rate reduced diffusion resistance, which promoted the reaction. The yield of DHB was 1.7% at a stirring rate of 1460 r/min, almost twice that without stirring. However, the membrane tube might not effectively contact the reaction solution at higher stirring rates. Therefore, the optimum stirring rate was 1460 r/min.

3.3.2. Effect of oxygen flow rate

The yield of DHB increased with oxygen flow rate, as illustrated in Fig. 7. When the oxygen flow rate was raised from 30 to 150 ml/min, the yield of DHB increased from 1.4% to 2.0%, indicating an increased oxygen flow rate could promote hydroxylation. However, a higher oxygen flow rate required higher operating pressure. As a result, 150 ml/min was selected as a suitable oxygen flow rate for the reaction.

3.3.3. Effect of catalyst concentration

Figure 8 shows the effect of catalyst concentration on phenol hydroxylation. As the catalyst concentration was increased up to 48.8 g/L, the yield of DHB increased from 1.1% to 2.1%. However, as the catalyst concentration was increased further to 53.8 g/L, the yield of DHB decreased to 1.6%. This is possibly

Fig. 7. Effect of oxygen flow on the yield of DHB. Reaction conditions: stirring rate 1460 r/min, catalyst concentration 43.8 g/L, ascorbic acid concentration 40 g/L, acetic acid concentration 60%.

Fig. 8. Effect of catalyst concentration on the yield of DHB. Reaction conditions: stirring rate 1460 r/min, oxygen flow 150 mL/min, ascorbic acid concentration 40 g/L, acetic acid concentration 60%.

because the catalyst particles did not mix effectively with the reaction solution at higher catalyst concentration. The optimum catalyst concentration was therefore 48.8 g/L.

3.3.4. Effect of ascorbic acid concentration

In phenol hydroxylation with oxygen, reducing agents such as ascorbic acid, H_2 and CO are needed to activate oxygen in the reaction system. Ascorbic acid is the most effective reducing agent in benzene hydroxylation with oxygen over Cu catalysts [13]. Therefore, we chose ascorbic acid as the reducing agent in phenol hydroxylation. Figure 9 shows the effect of ascorbic acid concentration on phenol hydroxylation. As the ascorbic acid concentration was increased from 20 to 50 g/L, the yield of DHB increased from 1.3% to 2.2%. Further increasing the concentration of ascorbic acid had no obvious effect on the yield of DHB, possibly because the excess ascorbic acid did not directly take part in the reaction because it was oxidized to dehydroascorbic acid [10,14]. It has been reported that excess ascorbic acid might decrease both the reactive oxygen species and yield of DHB [13,15]. Thus, the optimum ascorbic acid concentration was 50 g/L.

Fig. 9. Effect of ascorbic acid concentration on the yield of DHB. Reaction conditions: stirring rate 1460 r/min, oxygen flow 150 ml/min, catalyst concentration 48.8 g/L, acetic acid concentration 60%.

3.3.5. Effect of acetic acid concentration

In phenol hydroxylation over Cu catalysts, the concentration of acetic acid determines the amount of Cu leaching [16]: when the concentration of acetic acid is less than 40% (by volume), Cu readily leaches. However, when the concentration of acetic acid is 40%–60%, the amount of Cu leaching obviously decreased, and it was minimal at acetic acid concentrations above 80%. It has been reported that the synthesis of phenol is affected by the reduction of Cu^{2+} to Cu^+ , which could be restrained in a strong acid medium, although this was not beneficial for benzene hydroxylation [17].

The influence of acetic acid concentration on the yield of DHB after reaction for 90 min is presented in Fig. 10. The yield of DHB related to the acetic acid concentration followed the order: 0% > 80% > 20% > 60% > 40% > 100%, which might be for the following reasons. When the concentration of acetic acid was below 40%, many CuO particles leached into the reaction solution, so more free Cu^{2+} ions were present. These Cu^{2+} ions were readily reduced to Cu^+ , so the yield of DHB was higher at lower acetic acid concentration [17]. As the concentration of acetic acid was increased, the amount of leached Cu rapidly

Fig. 10. Effect of acetic acid concentration on the yield of DHB. Reaction conditions: stirring rate 1460 r/min, oxygen flow 150 ml/min, catalyst concentration 48.8 g/L, ascorbic acid concentration 50 g/L.

Fig. 11. SEM images of the surface and cross-sections of fresh membrane (a, c) and used membrane (b, d).

decreased and the CuO species on the support became the active sites for hydroxylation. A higher acetic acid concentration restrained Cu leaching, resulting in more CuO species on the support and a higher yield of DHB. When the concentration of acetic acid was increased to 100%, the reduction of Cu^{2+} to Cu^+ was restrained, leading to a lower yield of DHB. The amount of Cu in the reaction solution after the reaction measured by inductively coupled plasma spectrometry was 0.19 and 0.049 g for acetic acid concentrations of 0% and 80%, respectively, indicating that Cu leaching occurred readily at lower concentrations of acetic acid. Taking into account the recycling of catalyst, the optimum acetic acid concentration was 80%.

According to the above analysis, the optimal operating conditions for phenol hydroxylation with oxygen are as follows: stirring rate of 1460 r/min, oxygen flow of 150 ml/min, catalyst concentration of 48.8 g/L, ascorbic acid concentration of 50 g/L and acetic acid concentration of 80%. Under these operating conditions, the yield of DHB was 2.5%, which was lower than that obtained using a biomimetic catalyst [18]. However, compared with the biomimetic catalyst, the preparation of supported CuO catalyst was simple and the reaction conditions were mild. To further improve the yield of DHB, the catalyst preparation and use of a ceramic membrane distributor with smaller pore size should be investigated.

3.4. Membrane material stability

The stability of the ceramic membranes were investigated by observing the fresh and used membranes by FESEM, as shown in Fig. 11. The ceramic membrane surface did not change obviously and the thickness of the top layer of membrane remained about 30 μm after reaction. This indicates the ceramic membrane used in phenol hydroxylation possessed excellent thermal and chemical stability.

4. Conclusions

A CuO/TiO_2 catalyst was successfully prepared by impregnation for subsequent phenol hydroxylation with oxygen. The

Graphical Abstract

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Enhanced phenol hydroxylation with oxygen using a ceramic membrane distributor

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The membrane distributor could provide many small oxygen bubbles, increase the volumetric oxygen transfer coefficient and enhance the gas-liquid mass transfer, resulting in a higher dihydroxybenzene (DHB) yield.

CuO species interacted strongly with the TiO₂ support. A porous ceramic membrane was used as a distributor to control the supply of oxygen during phenol hydroxylation. Compared to the direct feeding mode, the membrane distributor increased both the volumetric oxygen transfer coefficient and the yield of DHB. The ceramic membrane also exhibited excellent thermal and chemical stability. These results suggest that a membrane distributor is an effective way to increase gas-liquid mass transfer that may be used in many reactions in addition to phenol hydroxylation with oxygen.

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陶瓷膜分布器强化氧气氧化苯酚羟基化反应

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摘要: 采用浸渍法制备CuO/TiO₂催化剂, 利用X射线衍射、透射电镜、程序升温还原等技术对催化剂进行了表征, 结果表明, CuO以分散态和晶体两种形式存在, 且与载体有强的相互作用。以陶瓷膜为分布器控制氧气的进料, 进行了CuO/TiO₂催化氧气氧化苯酚羟基化反应。与直接通入氧气方式相比, 采用孔径为0.5 μm的陶瓷膜控制进氧, 可使苯二酚收率提高13%, 这主要是由于采用陶瓷膜作为氧气进料分布器可以提供大量具有微小尺寸的氧气气泡, 提高体积溶氧系数, 增强气液传质效果。在优化的反应条件下, 苯二酚收率达2.5%。对使用后的陶瓷膜进行扫描电镜表征, 发现陶瓷膜具有良好的稳定性。

关键词: 苯酚; 羟基化; 氧气; 陶瓷膜; 膜分布器

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1. 前言

苯二酚是重要的化工原料^[1]. 苯酚羟基化制备苯二酚是一种绿色合成工艺, 该法以苯酚为原料, 经过氧化物氧化生成邻、对苯二酚, 克服了传统方法规模小、反应过程“三废”多等缺点, 受到广泛关注. 苯酚羟基化法的氧化剂主要有双氧水^[2,3]、氧气^[4]等. 其中氧气价格低廉、来源广泛, 无环境污染, 是优选的氧化剂用于苯酚羟基化反应时, 可避免深度氧化, 具有原子经济性.

氧气作为氧化剂进行苯酚羟基化反应的关键在于对氧气进行活化产生活性氧, 并且提高它在反应体系中的分散度、加强传质. 多孔陶瓷膜具有大量规整的微米或纳米级孔道, 利用多孔陶瓷膜作为气体进料分布器, 可以提供大量具有微小尺寸的氧气气泡, 提高反应器中的气液传质效果, 促进反应的进行. Coronas等^[5]将陶瓷膜作为气体分布器, 用于甲烷的氧化偶联反应, 相比固定床反应器, 反应的选择性得到了很大的提高. 在本课题组前期工作中^[6], 利用陶瓷膜作为双氧水的进料分布器进行分子筛催化苯酚羟基化制苯二酚, 可明显提高产物选择性. 而采用陶瓷膜作为氧气分布器进行苯酚羟基化反应还未见报道.

本文采用浸渍法制备CuO/TiO₂催化剂, 并使用X射线衍射(XRD)、透射电镜(TEM)、程序升温还原(TPR)等技术对其微结构进行表征, 并尝试将多孔陶瓷膜用作氧气分布器进行CuO/TiO₂催化苯酚羟基化反应, 强化物料的传质效果, 提高反应收率. 采用亚硫酸盐法研究膜分布器对反应器中体积溶氧系数的影响, 然后考察苯酚羟基化体系中膜分布器的加入对反应的影响, 并对反应条件进行了优化.

2. 实验部分

2.1. 催化剂的制备与表征

铜催化剂被广泛用于有机合成, 特别是液相氧化反应体系中^[7-10]. 据报道, 高分散的铜是进行苯酚羟基化的活性中心^[10]. 本文采用浸渍法制备CuO/TiO₂催化剂, 并用于氧气氧化苯酚羟基化反应. 称取一定量的三水硝酸铜(AR, 上海新宝精细化工)及锐钛矿TiO₂载体(青岛攀枝花钛业公司)加入50 ml水中, 磁力搅拌8 h后, 利用旋转

蒸发仪蒸干水分, 并在373 K干燥, 研磨后于673 K煅烧5 h, 制得的催化剂记为CuO/TiO₂, 其中Cu含量为7%.

采用德国Bruker公司D8-Advance型X射线分析仪对催化剂进行XRD表征, Cu K_α射线, 扫描速率0.2°/s, 管电压40 kV, 管电流30 mA. TPR实验在日本BEL公司的BELCAT-A型化学吸附仪上进行, 样品先在573 K用Ar气吹扫2 h, 冷却至323 K, 然后在10%H₂/Ar气氛中, 以10 K/min升温至1023 K. 采用日本JEOL公司的JEM-2011(HR)型TEM表征催化剂的形貌, 样品置于乙醇溶液中超声分散, 其悬浮液滴加到覆有铜网的碳膜上晾干后进行测试.

2.2. 苯酚羟基化

氧气氧化苯酚羟基化反应在如图1所示的反应器内进行. 反应器主要包括恒温水浴槽、反应器、膜组件、流量计和氧气钢瓶等. 玻璃反应器的体积为250 ml. 陶瓷膜(由江苏久吾科技股份有限公司提供)的内外径分别为8和12 mm, 长度为6 cm; 膜的一端采用釉封密封, 氧气由另一端进入膜中, 再经膜孔出与反应液接触并反应, 氧气流速由转子流量计控制.

称取一定量的抗坏血酸(AR, 国药集团化学试剂有限公司)、CuO/TiO₂催化剂、20 ml苯酚(AR, 国药集团化学试剂有限公司)以及200 ml不同体积浓度醋酸(AR, 上海申博化工有限公司)水溶液(200 ml)加到反应器中, 加热至308 K, 利用陶瓷膜分布进料氧气, 反应90 min后取样分析.

反应液稀释后用Aglient 1200型高效液相色谱分析, 并采用外标法测定苯酚、苯二酚浓度. 分析条件为: 色谱柱, ZORBAX Eclipse XDB-C18, 250×4.6 mm; 柱温303 K, 流动相为V(甲醇): V(水)=40:60; 流速1 ml/min, 检测波长277 nm, 进样量5 μl.

陶瓷膜的微结构采用日本JEOL公司S-4800型场发射扫描电镜(SEM)表征.

3. 结果与讨论

3.1. 催化剂的物性表征

3.1.1. XRD结果

图2为CuO/TiO₂和TiO₂样品的XRD谱. 可以看出, 与载体TiO₂相比, CuO/TiO₂在2θ = 35.5°, 39.0°处明显多出

两个衍射峰,分别对应于单斜相氧化铜的(-111)和(111)晶面,但其衍射峰强度较弱,可能是由于氧化铜粒径小或结晶度较低所致。

3.1.2. TEM结果

图3为CuO/TiO₂催化剂的TEM及HRTEM照片。由图可见, TiO₂载体表面上比较松散地排布有颗粒状物质,从内插图可以看到这种颗粒状物质为晶体,颗粒尺寸在3.0 nm左右,且晶格间距为0.186 nm的晶格条纹呈周期性出现,对应于氧化铜(-202)晶格面的晶格间距,说明在TiO₂载体表面负载了氧化铜晶体,且分散得较好。

3.1.3. TPR结果

图4显示了CuO/TiO₂催化剂的TPR谱。由图可见,样品在443, 541和610 K处出现明显的特征峰,且后二者峰面积明显高于前者。Lasson等^[11]研究了CuO/TiO₂催化剂TPR谱,发现453 K处还原峰对应于单层分散态氧化铜的还原; 503~553 K处还原峰对应于晶体氧化铜的还原。因此,可将样品位于443 K处还原峰对应于单层分散态氧化铜的还原; 541 K处为晶体氧化铜的还原; 610 K处可能为与载体具有更强相互作用的晶体氧化铜的还原。由此可知, TiO₂载体上负载的氧化铜以晶体与单层分散态两种形式存在,且以前者形式为主。

3.2. 膜分布器对苯酚羟基化反应的影响

采用亚硫酸盐法^[12]测定了使用膜分布器后反应体系中体积溶氧系数,并与直接通入氧气(采用聚氨酯(PU)管进料)进行对比,结果如表1所示,使用氧化铝陶瓷膜(孔径为0.5 μm)或莫来石陶瓷膜(孔径1 μm)作为膜分布器进氧时,反应器内体积溶氧系数约是直接通入氧气方式的8倍。这主要是由于利用多孔陶瓷膜作为分布器进氧,减小了氧气泡直径,增加了气液传质面积,从而提高氧气在反应液中的传质能力。

图5为采用氧化铝陶瓷膜和莫来石陶瓷膜作为氧气分布器进行苯酚羟基化反应结果,并与直接通入氧气进行比较。由图可见,使用两种陶瓷膜分布器均可提高苯二酚收率,特别是利用孔径为0.5 μm的氧化铝陶瓷膜时,苯二酚收率提高了13%。图6为对搅拌速度的影响。可以发现在实验范围内,增加搅拌速度可明显提高苯二酚收率,因此,扩散控制是该反应过程的控制步骤。结合表1可以看出,在反应器中引入膜分布器,可以明显提高体积溶氧系数,强化氧气在反应液中的传质能力。这是苯二酚收率增加的主要原因。还可以看出,随反应时间的延长,苯酚转化率基本呈现上升趋势,而苯二酚选择性逐渐下降(结果未显示),总体上苯二酚收率先上升后趋于稳定。

苯二酚选择性下降主要是由于其深度氧化成苯醌或其它副产物所致^[6]。引入膜分布器后,苯二酚收率的增加程度小于体积溶氧系数的增加程度,说明还有其他因素,如搅拌速度、氧气流量等影响苯酚羟基化反应过程。小孔径的膜作为分布器时更有利于苯二酚的生成,但进一步减小膜孔径,导致膜分布器的操作压力显著增加,故选择孔径为0.5 μm比较适宜。

3.3. 反应参数对氧气氧化苯酚羟基化反应的影响

3.3.1. 搅拌速度的影响

图6为搅拌速度对苯酚羟基化反应的影响。由图可见,随着搅拌速度的提高,苯二酚收率随之倍加,说明提高搅拌速度减少了气液固之间的扩散阻力,促进了反应的进行。当搅拌速度为1460 r/min时,苯二酚收率为1.7%,比无搅拌时的提高了近2倍。进一步提高转速,在反应器中心出现漩涡,导致膜与反应液不能充分接触。因此,选择搅拌速度为1460 r/min。

3.3.2. 氧气流量的影响

图6为氧气流量对苯二酚收率的影响。由图可见,当氧气流量从30提高到150 ml/min时,苯二酚收率从1.4%提高到2.0%,说明增加氧气流量有利于反应的进行。但继续提高氧气流速,氧气透过膜需要更高的压力,考虑到实际操作条件,故氧气流量宜为150 ml/min。

3.3.3. 催化剂浓度的影响

图8为催化剂浓度对苯酚羟基化反应的影响。由图可见,当催化剂浓度低于48.8 g/L时,苯二酚收率随着催化剂浓度的增加由1.1%逐渐增至2.1%;至53.8 g/L时,反而降至1.6%。这可能是由于当催化剂过量时,它与反应物无法充分混合,故选择催化剂浓度为48.8 g/L。

3.3.4. 抗坏血酸浓度的影响

氧气氧化苯酚羟基化反应体系需加入还原剂来活化氧,如抗坏血酸、氢气、一氧化碳等。以铜为催化剂进行氧气氧化苯酚羟基化反应时,抗坏血酸被认为是最有效的还原剂^[13]。本文也考察了抗坏血酸浓度对苯二酚收率的影响,结果见图9。可以看出,随着抗坏血酸浓度从20.0增加到50.0 g/L,苯二酚收率从1.3%提高到2.2%;至60.0 g/L,苯二酚收率变化不大,这是由于多余的抗坏血酸并未直接参与反应,而被氧化为脱氢抗坏血酸^[10,14]。也有人认为,多余的抗坏血酸会降低活性氧种类,不利于苯二酚生成^[13,15],故选择抗坏血酸浓度为50.0 g/L。

3.3.5. 醋酸浓度的影响

采用铜系催化剂进行苯酚羟基化反应时,催化剂活性组分的流失量与醋酸浓度有关^[16]。通常醋酸体积浓度

低于40%, 活性组分的流失量维持在一个较高的水平; 当醋酸浓度为40%~60%时, 活性组分流失量迅速下降; 至80%~100%时活性组分流失量最小. 苯酚的生成与 Cu^{2+} 还原为 Cu^+ 的过程有关^[17], 在强酸的环境下会抑制该还原过程的发生, 不利于苯羟基化反应进行.

图10为反应90 min时苯二酚收率随醋酸浓度的变化. 由图可见, 不同醋酸浓度时苯二酚收率大小顺序为: 0%>80%>20%>60%>40%>100%. 这可能是由于膜分布器的加入使得反应器内的传质能力提高, 从而促进反应进行; 同时由于醋酸浓度低于40%时, 大量氧化铜从载体上流失到反应液中, 从而形成游离态的 Cu^{2+} , 后者更容易被还原, 因此低浓度的醋酸有利于苯二酚的生成^[17]; 当醋酸浓度增加, 活性组分流失量迅速下降, 此时载体上活性组分成为催化反应进行的活性中心, 由于高浓度的醋酸阻止活性组分流失, 因此苯二酚收率随醋酸浓度增加而增加. 当醋酸浓度达到100%时, 由于强酸对 Cu^{2+} 还原的抑制作用, 导致苯二酚收率降低. 当醋酸浓度为0%和80%时, 反应后的反应液中铜含量分别为0.19和0.049 g (ICP测定), 说明醋酸浓度低时, 氧化铜流失量较为严重. 为了实现催化剂重复利用, 故选择醋酸浓度为80%的水溶液作为溶剂进行反应.

综上所述, 优化的陶瓷膜分布器强化氧气氧化苯酚羟基化反应条件为: 搅拌速度1460 r/min, 氧气流量150 ml/min, 催化剂浓度48.8 g/L, 抗坏血酸浓度50.0 g/L, 醋酸浓度80%. 此时苯二酚收率达2.5%, 低于仿生催化剂^[18]等的. 但本文催化剂制备过程简单, 反应操作条件温和. 为进一步提高苯二酚收率, 下一步工作将围绕催化剂研制及更小孔径陶瓷膜分布器的使用等方面展开研究.

3.4. 膜材料的稳定性

为了考察陶瓷膜稳定性, 对新鲜的及使用后的膜进行SEM表征, 结果见图11. 可以看出, 使用后膜面没有明显的变化, 膜厚度基本维持在30 μm 左右, 说明在反应体系中, 陶瓷膜材料作为氧气分布器时具有良好的稳定性.

4. 结论

利用浸渍法制备了氧气氧化苯酚羟基化反应用催化剂 CuO/TiO_2 , CuO 与 TiO_2 之间的相互作用强. 与传统通入氧气方式相比, 采用多孔陶瓷膜作为苯酚羟基化的氧气进料分布器, 可明显提高体积溶氧系数, 从而增加苯二酚收率. 反应过程中陶瓷膜具有良好的稳定性. 膜分布器是一种有效的增强气液传质的操作方式, 在氧气氧化苯酚羟基化反应等体系中具有潜在的应用前景.