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High catalytic performance of CuO nanocrystals with largest defects

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Abstract−To improve the calalytic performance of CuO, nanometer-sized CuO particles were prepared with ultrafiltration surface contact method (UMSCM). X-ray powder diffraction (XRD) and scanning electron microscopy (SEM) were used to characterize the crystal structure and morphology of the particles made with UMSCM, hydrothermal method, grounding method as well as a commercial one. SEM results illustrate that UMSCM prepared CuO particles mainly show the form of orthorhombic sliced crystals with the largest amounts of defects compared to CuO particles made by the other three methods. In the oxidation of cumene, CuO prepared with UMSCM also shows better catalytic performance than the other three particles, which can be ascribed to its smaller particle sizes and larger defects so as to accelerate the surface adsorption rate of O_2 molecules and the diffusion of ions and atoms, thus improving the catalytic activity.

Key words: Ultrafiltration, Membrane, Nano-sized CuO, Reaction of Cumene Oxidation, Catalytic Performance

INTRODUCTION

Since Hercules and British Petroleum (BP) developed the method for manufacturing phenol and acetone from cumene in the 1940's, it has been substantially improved and it has become a commonly used technology for commercial production of phenol. At present, more than 90% of phenol in the world is produced through this approach. In this process, a key intermediate step is the oxidation of cumene in which cumene hydroperoxide is formed. The traditional method is a self-catalytic reaction in which cumene hydroperoxide (CHP) itself is inducer and air as oxidant. After that, a great deal of research has been conducted on the catalytic role of cumene oxidation reaction in heterogeneous systems to overcome the shortcomings of low conversion rate, low selectivity and safety issue [1]. Recently, CuO nano-sized particles as catalyst for the cumene oxidation reaction [2-6] have attracted considerable interest because of their lower reaction temperature, higher conversion rate and higher selectivity.

To meet the need of catalytic performance, nano-sized, monodispersed, large ratio of surface area to volume and high catalytic activity of CuO particles are desirable. Generally, CuO particles can be made by two steps: in the first step $Cu(OH)_2$ colloid are made; and crystalline CuO particles are obtained by dehydration of the formed $Cu(OH)_2$. In the second step, several methods such as hydrothermal, grounding, ultrasonic and precipitation are used to minimize the prepared CuO particle size [7-12]. A key point for reducing CuO particle size is to reduce the aggregation of $Cu(OH)_2$ and to prevent the further growth of formed colloids.

Ultrafiltration (UF) membranes have relatively uniform pore sizes. A micro-phase reaction condition will be formed on membrane surface when fluid flows through pores of the membrane under a tangential force. Based on this principle, membranes have been used to prepare emulsions with uniformly dispersed droplets [13], highly dispersed polymeric colloids [14] and poly-aluminum chloride clusters [15] etc. Particles obtained with this method have smaller sizes and better uniformity than that with the traditional high pressure homogeneous reaction method. It was found that the relationship between droplet diameter and membrane pore size is nearly linear [16]. The diameter of a droplet is generally 2-10 times of the pore size of the membrane. The method of controllably feeding reactants to reaction zones using membranes has been successfully applied to the preparation of catalysts. Therefore, the aggregation of $Cu(OH)_2$ can be controlled with membranes, thereby obtaining smaller sized high performance catalysts.

This paper reports a superior method of ultrafiltration membrane (UMSCM) for preparing nano-sized CuO crystals. In detail, a $Cu(NO_3)_2$ solution permeates through a polyethersulfone membrane with an average pore size of 25 nm under a certain pressure across the membrane. Nano-sized CuO particles are then formed when $Cu(NO_3)_2$ solution reacts with NaOH flowing solution on a polyethersulfone hollow fiber membrane surface. The effects of membrane preparation conditions on CuO particle size, morphology as well as catalytic performance for cumene oxidation reaction are also investigated. Based on a similar method reported in the literature, CuO was also prepared with hydrothermal [17] and grounding methods [18].

EXPERIMENTAL SECTION

1. Materials

Cupric nitrate, sodium hydroxide, cupric oxide and cumene, all analytical grade, were purchased from Aldrich and used without further purification. The polyethersulfone (number average molecular weight of 40000) hollow fiber membrane was self-made, and the average pore size of the membrane is about 25 nm, which was measured with an atomic force microscope (AFM). The inner diameter of the hollow fiber membrane is 2.0 mm, and the outer diameter is 2.7 mm. The effective length of the membrane is 40 cm and

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surface area is 0.02 m^2.

2. Preparation of Nano-sized CuO Particles

Certain amounts of NaOH and $Cu(NO_3)_2 \cdot 3H_2O$ were weighed and dissolved into distilled water and the solution was maintained at 30 °C, respectively. Then the as-prepared NaOH solution was pumped into the lumen side of a polyethersulfone hollow fiber membrane and the $Cu(NO_3)_2$ solution to the shell side. The pressure difference across the membrane was controlled at 0.04 MPa, with the pressure of shell side higher than the lumen side. So $Cu(NO_3)_2$ solution permeated through the pores of membrane and dispersed into NaOH solution by micro-droplets. As the NaOH solution flowed on the membrane surface, the shear force make $Cu(OH)_2$ formed on membrane surface and dispersed into the NaOH solution as colloids. The reaction solution was then transferred into a water-jacketed vessel for crystallization for 24 hours at 60 °C, followed by cooling, then water washing to pH=7.0. Solid grey powder was obtained after filtration and then drying at 60 °C. The CuO prepared with hydrothermal and grounding methods was conducted as previously described [17,18].

3. Characterization of CuO

CuO crystals were characterized with X-ray diffract meter, XRD-6000 (Shimadzu, Japan). Copper target: particle morphology was characterized with S-4700 scan electron microscope (SEM, Hitachi, Japan). Magnesium target: surface area was measured with a surface area and pore size meter (Beijing Analytical Instrument Co. Beijing, China).

4. Cumene Oxidation Reaction

The cumene oxidation reaction was performed in a three-necked flask with a reflux under atmospheric pressure in the temperature range of 70-110 °C by feeding oxygen bubbles into the reactant of cumene and no extra stirring was used. The composition of products was measured with GC-14B gas chromatograph (Shimadzu, Japan) equipped with flame ionization detector. The catalysts were used continuously to study the effect of various parameters, viz., catalyst type, UMSCM-prepared CuO dosage, oxygen concentration and reaction temperature.

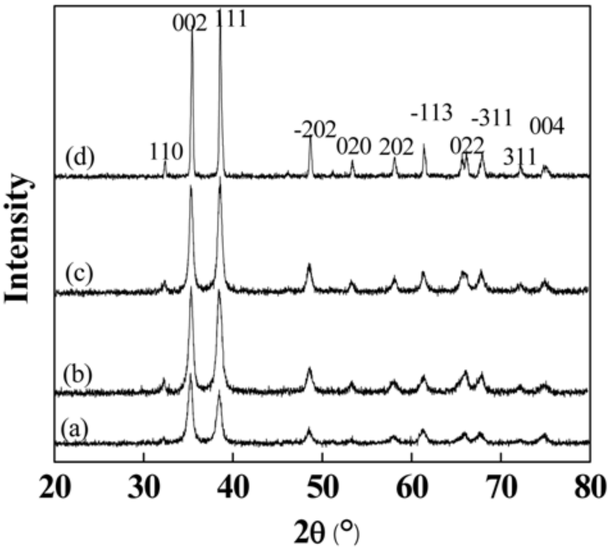

Fig. 1. XRD patterns of CuO particles prepared with different methods: (a) UF membrane surface contact method; (b) hydrothermal method; (c) grounding method; (d) commercial.

RESULTS AND DISCUSSION

1. XRD Analysis of Nano-sized CuO Particles

1-1. Effect of Different Preparation Methods

Fig. 1 shows the XRD patterns of commercial CuO and the CuO prepared with UMSCM, hydrothermal method, and grounding method. As shown in Fig. 1, the 2θ value of commercial CuO's XRD peak is nearly as same as that of CuO prepared with the other three methods. Reference to the JCPDS card indicates that all four types of crystals belong to orthorhombic crystals. Further, the peak intensity of commercial CuO is higher than that of CuO prepared with the other three methods, and the peak intensity of CuO prepared with the UMSCM is distinctly lower and broader. This result indicates that the particle size of the CuO made with UMSCM is smaller than that made by hydrothermal and ground methods, especially the commercial CuO. In addition, there are some defects in the crystals of the UMSCM-prepared CuO, reflected by broad diffraction. The size of the four types of crystals was calculated with Scheerer equation by taking the (III) crystal face diffraction characteristic peak. Their sizes are 144 nm, 50 nm, 32 nm, and 14 nm for commercial, grounding, hydrothermal and UMSCM, while the corresponding specific surface areas are 8.56, 18.57, 24.91 and 35.81 m^2/g, respectively.

1-2. Effect of Flow Rate

Fig. 2 shows the XRD patterns of CuO particles prepared with the different flow rates, and Fig. 3 shows variation of the particle size and specific surface area of UMSCM prepared CuO particles with flow rate. The experiment was conducted at a molar ratio of NaOH : $Cu(NO_3)_2$ equal to 4. As shown in Fig. 3, with increasing flow rate the particle size decreased and specific surface area increased for the CuO particles prepared with UMSCM. This phenomenon can be explained as that a higher flow rate, thus higher shear forces, leads to a smaller CuO colloid sizes and therefore larger specific surface areas. This result agrees with those reported by Joscelyne

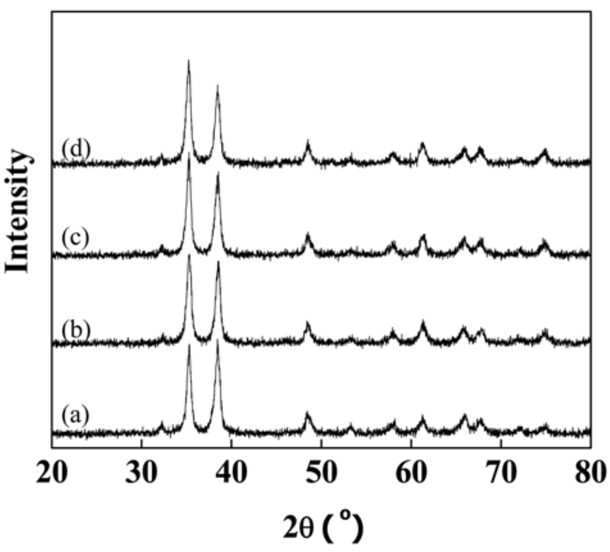

Fig. 2. XRD patterns of CuO particles prepared with different flow rate: (a) 0.3 m/s; (b) 0.7 m/s; (c) 1.2 m/s; (d) 1.5 m/s.

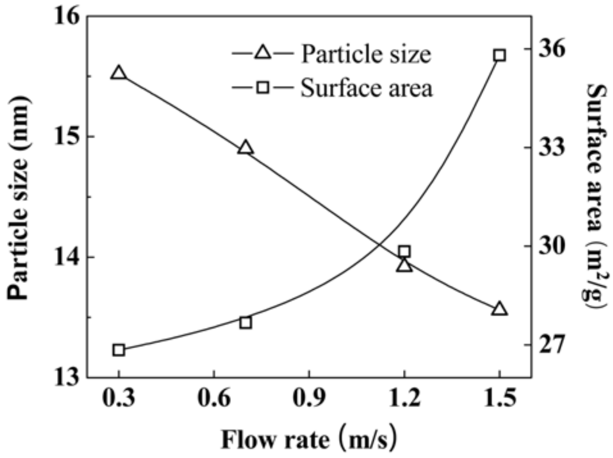

Fig. 3. Effect of flow rate on the effective diameter and the specific surface area of CuO particles prepared with UMSCM.

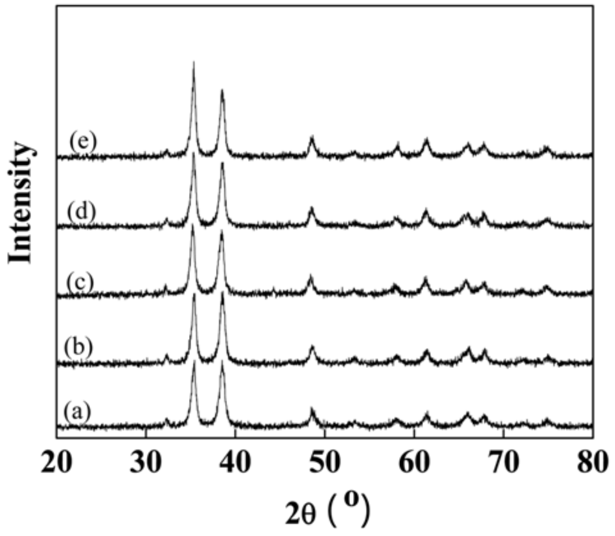

Fig. 4. XRD patterns of CuO particles prepared with different NaOH to $Cu(NO_3)_2$ molar ratio: (a) 2.5; (b) 3.5; (c) 4; (d) 4.5; (e) 5.5.

[19] and Hong [12].

1-3. Effect of NaOH to $Cu(NO_3)_2$ Molar Ratio

Fig. 4 shows the XRD patterns of CuO particles prepared with different NaOH to $Cu(NO_3)_2$ molar ratio, and Fig. 5 shows the variation of the particle size and specific surface area of UMSCM-prepared CuO particles with NaOH to $Cu(NO_3)_2$ molar ratio. The experiment was performed at a flow rate of 1.2 m/s. From Fig. 5, with increasing NaOH to $Cu(NO_3)_2$ molar ratio, the particle size decreased and specific surface area increased for the CuO particles prepared with UMSCM. This can be ascribed to the fact that a higher NaOH concentration can effectively restrain the aggregation and growth of $Cu(OH)_2$ colloids. As a result, the obtained particles would be smaller.

2. SEM Analysis Nano-sized CuO Particles

Fig. 6 shows the SEM pictures of the commercial and UMSCM made, hydrothermal method made and grounding method made CuO particles. As illustrated by Fig. 6, the commercial CuO is present in large aggregates with an average diameter over 200 nm. The CuO prepared by UMSCM and hydrothermal method is present in crystals. Compared to CuO made by the hydrothermal method, the CuO particles made by UMSCM have smaller size and thus larger specific surface area. The CuO prepared by the grounding method is present in non-spherical aggregates.

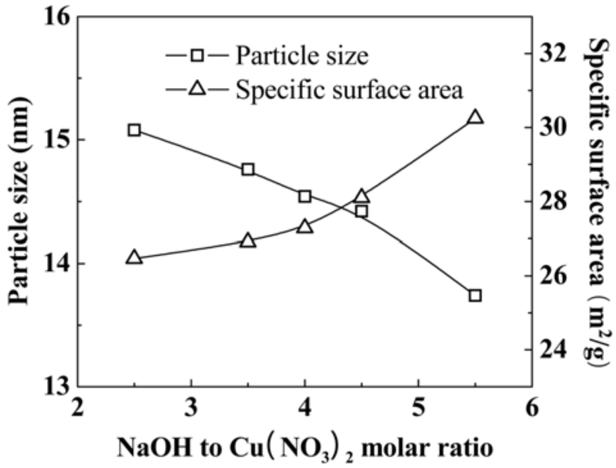

Fig. 5. Effect of NaOH to $Cu(NO_3)_2$ molar ratio on the effective diameter and specific surface area of CuO particles prepared with UMSCM.

3. Catalytic Performance of Nano-sized CuO Particles in Cumene Oxidation Reaction

3-1. Catalytic Performance of CuO Prepared with Different Methods

To study the catalytic role of the CuO prepared by UMSCM on cumene oxidation, a cumene oxidation reaction was performed with the above-mentioned four types of CuO with the same dosage of 0.01 g/mL, enriched oxygen air as oxidant (28.8% oxygen), and reaction temperature of 90 °C. The experimental data in Fig. 7 demonstrate the order of CHP yield for the four catalysts (based on accumulated CHP wt% at reaction time of 12 hours): UMSCM prepared CuO (31.22 wt%)>hydrothermal CuO (27.32 wt%)>grounding CuO (23.84 wt%)>commercial CuO (20.57 wt%). This is because the activities of the catalysts are controlled by their particle sizes and defects [20]. The defect of p-type semiconductor oxidant CuO is mainly in the vacancy of the copper ion in the cation sub-lattice, which accelerates the surface adsorption rate of O_2 molecules through defects. Defects are beneficial to the diffusion of ions and atoms, which enhances catalytic activity. As shown in Fig. 1, the three types of CuO except commercial CuO have large amounts of defects. As a result, these three types of CuO have higher catalytic activity than the commercial one. Among them, the CuO prepared by UMSCM has the smallest particle sizes and thickness. Therefore, it has the largest specific surface area and thus the highest activity. It was calculated that the catalytic performance of this catalyst is 52.13% higher than the commercial CuO, 31.13% higher than the grounding CuO and 14.4% higher than the hydrothermal CuO.

3-2. Effect of UMSCM Prepared CuO Dosage

The effect of the amount of catalyst on cumene oxidation reaction was studied by calculating the accumulated CHP concentration at a reaction time of 12 hours. The experiment was performed at 90 °C using oxygen-enriched air (28% oxygen) and UMSCM pre-

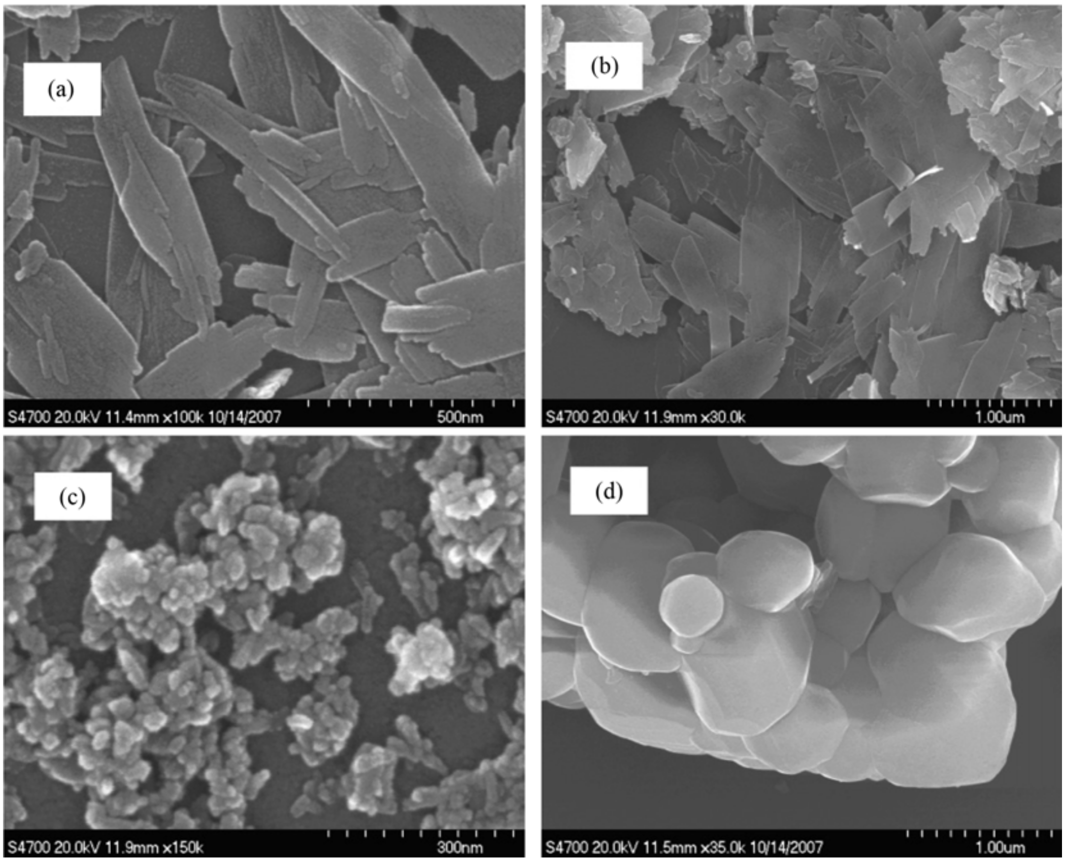

Fig. 6. SEM images of CuO crystals prepared with: (a) UMSCM, (b) hydrothermal method, (c) grounding method and (d) commercial.

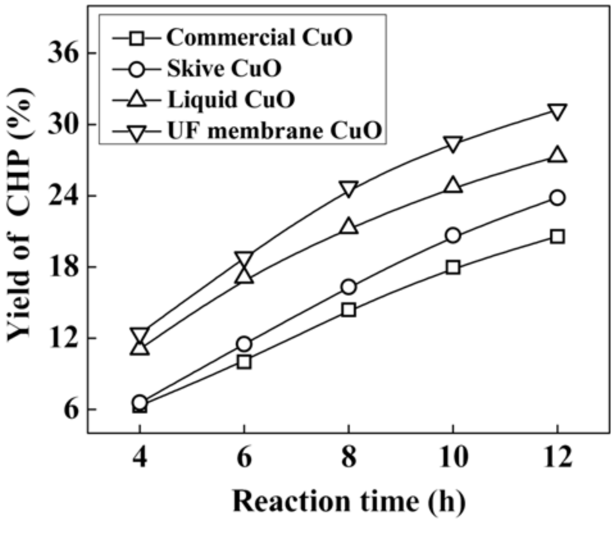

Fig. 7. Effect of catalyst type on yield of CHP in the reaction of cumene oxidation, catalyst dosage is 0.01 g/mL, reaction temperature is 90 °C, reaction time is 12 h, oxygen concentration is 28.8 wt%.

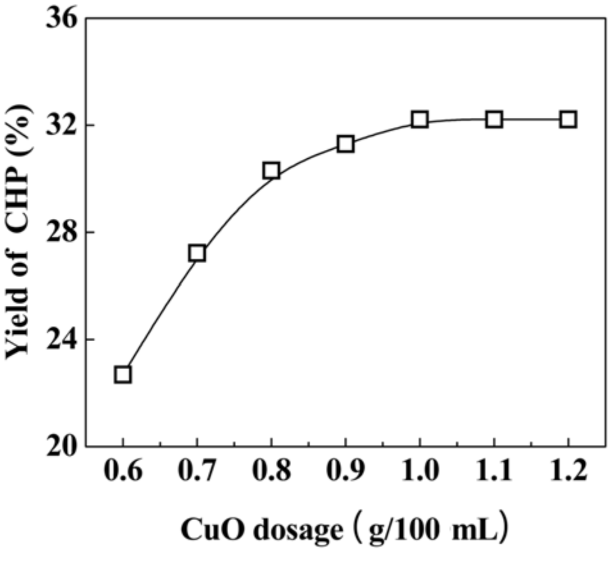

Fig. 8. Effect of UMSCM-prepared CuO dosage on yield of CHP in the reaction of cumene oxidation, reaction time is 12 h, reaction temperature is 90 °C, oxygen concentration is 28.8 wt%.

pared CuO as catalyst. The experimental result is shown in Fig. 8.

The cumene oxidation reaction for preparing CHP is a free-radical chain reaction. As shown in Fig. 8, the accumulated CHP concentration increases with increasing the amount of catalyst. This is caused by the increased number of catalysis centers on the catalyst surface and thus an increase in conversion rate from cumene to CHP. This effect becomes less significant when the amount of catalyst exceeds 0.01 g/mL. Therefore, the catalyst usage for the UF-membrane prepared CuO was set at 0.01 g/mL.

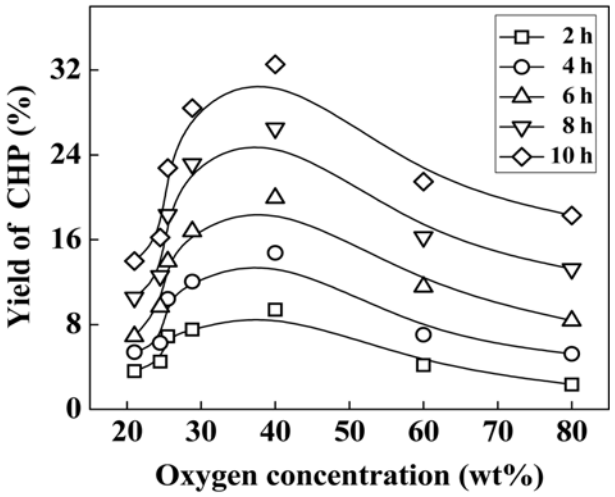

Fig. 9. Effect of oxygen concentration on the yield of CHP in the reaction of cumene oxidation, reaction time is from 2 h to 10 h, reaction temperature is 90 °C, UMSCM prepared CuO as catalyst and catalyst dosage is 0.01 g/mL.

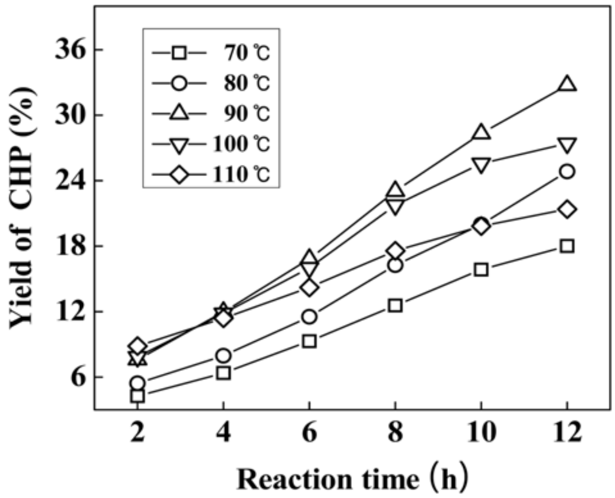

Fig. 10. Effect of reaction temperature on the yield of CHP in the reaction of cumene oxidation, UMSCM prepared CuO as catalyst, catalyst dosage is 0.01 g/mL, oxygen concentration is 28.8 wt%.

3-3. Effect of Oxygen Concentration

Fig. 9 shows the effect of oxygen concentration on catalysis performance of UMSCM prepared CuO in cumene oxidation reaction at 90 °C. The results demonstrate that the CHP yield increases significantly with increasing oxygen concentration at the beginning of the reaction. This is due to the increased O_2 solubility at a higher oxygen concentration, which in turn increases reaction rate. However, the reaction rate was increased more rapidly after a reaction time of 6 hours with oxygen concentration of 21%. The time for reaching a high reaction rate was significantly reduced with increasing oxygen concentration. This result is a reflection of the catalytic role of CuO catalyst. The oxidation reaction rate was slow at a low O_2 concentration, and the self-catalysis was weak because the CHP concentration was low. As the reaction proceeded, CHP concentration increased gradually, and the self-catalysis became stronger. The reaction rate was significantly increased due to the presence of both self-catalysis and the catalysis of CuO. At a high oxygen concentration CHP concentration increases rapidly, which enhances the self-catalysis role of CHP. Therefore, an increase in oxygen concentration results in a significant increase in reaction rate. As shown in Fig. 8, the accumulated CHP concentration is 28 wt% after 10 hours. This concentration is twice as high as that obtained in the conventional oxidation reaction with air.

Fig. 9 illustrates that at an oxygen concentration below 40 wt% the CHP concentration increases with increasing oxygen concentration. However, the increase in CHP concentration slows down at an oxygen concentration above 28.8 wt%. In addition, the CHP concentration decreases at an oxygen concentration greater than 40 wt%. Table 1 shows that under the catalysis of CuO the conversion rate in the oxidation reaction increases but the selectivity decreases with increasing oxygen concentration. The selectivity change is not very obvious with 29 wt% oxygen, but it becomes more significant when the oxygen concentration exceeds 40 wt%. This indicates that 29 wt% oxygen is the optimal concentration for the catalytic reaction from cumene to CHP. This oxygen concentration can be easily achieved with membrane filtration. The membrane enriched oxygen concentration is typically 28-31%. Therefore, the combination of membrane enriched oxygen and UF-membrane-prepared CuO is suitable to the cumene oxidation reaction.

3-4. Effect of Reaction Temperature

The effect of reaction temperature on oxidation reaction was investigated using CuO catalyst prepared by UMSCM, enriched air

Table 1. Effect of oxygen concentration on conversion rate, CHP selectivity and product concentration

Oxygen concentration (%)	Products concentration			Conversion rate (%)	CHP selectivity (%)
	CHP (wt%)	AP[a] (wt%)	PP[b] (wt%)		
21	17.34	0.85	Trace	18.20	95.26
24.5	19.61	1.06	Trace	20.67	94.87
25.5	27.21	1.46	Trace	28.77	94.56
28.8	28.41	1.49	0.51	30.41	93.42
40	32.55	1.79	0.72	35.06	92.84
60	25.59	2.29	1.38	29.26	87.44
80	22.63	3.93	2.18	28.74	78.73

[a] Acetophenone

[b] Dimethylphenyl carbinol

Table 2. Effect of temperature on conversion rate, CHP selectivity and product concentration

Temperature (°C)	Products concentration			Conversion rate (%)	CHP selectivity (%)
	CHP (wt%)	AP (wt%)	PP (wt%)		
70	18.02	0.99	trace	19.01	94.78
80	24.85	1.69	trace	26.54	93.61
90	32.74	2.47	trace	35.21	92.92
100	27.41	3.25	0.7	31.36	87.40
110	21.38	4.78	1.9	28.06	76.19

(28.8 wt% oxygen) as oxidant, and at reaction temperatures of 70 °C, 80 °C, 90 °C, 100 °C, and 110 °C, respectively.

As shown in Fig. 10, there was no noticeable induction time after the catalyst was added, but the reaction was slow under 70 °C. The reaction rate is accelerated at higher temperatures, which is beneficial to the conversion and CHP yield. The results in Table 2 demonstrate that the amounts of by-products increased at higher temperatures too, i.e., lower selectivity. The amounts of by-products become more significant at a reaction temperature greater than 100 °C. At this condition, the CHP selectivity is lower than 90%. Moreover, over-high temperature decreases the O_2 solubility in the reaction solution, therefore affecting reaction rate. The optimal temperature for the CuO catalysts prepared by UMSCM is 90 °C. At this temperature, the concentration is 28 wt% at a reaction time of 10 hours and the CHP selectivity is 92.92%.

CONCLUSIONS

The CuO prepared by UMSCM is present in orthorhombic sliced crystals. Increasing flow rate and NaOH to $Cu(NO_3)_2$ molar ratio leads to increased specific surface areas of the formed CuO crystals. The particle sizes are 144 nm, 50 nm, 32 nm, and 14 nm for commercial CuO and the CuO prepared with grounding, hydrothermal and UMSCM, respectively. The corresponding specific surface areas are 8.56, 18.57, 24.91, 35.81 m^2/g, respectively. The CuO prepared by UMSCM exhibits excellent catalytic performance for cumene oxidation reaction. At an optimal condition of 28.8 wt% oxygen, catalyst dosage of 0.01 g/mL, and temperature of 90 °C, the catalytic effectiveness of the CuO catalyst prepared by UMSCM is 52.13% higher than the commercial CuO , 31.13% higher than the grounding CuO and 14.4% higher than the hydrothermal CuO. The oxygen concentration of 28-31% is suitable for the catalytic conversion from cumene to CHP. The cumene oxidation reaction with membrane enriched oxygen and UMSCM CuO has high conversion rate, high selectivity, and low reaction temperature. Therefore, membrane enriched oxygen together with UMSCM prepared CuO catalyst is an ideal combination for cumene oxidation reaction.

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