


# Study on the oxidation of vanillymandelic acid to vanillin over mesoporous copper oxide

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**Abstract** Mesoporous CuO synthesized by the hydrothermal method was used as a catalyst for the oxidation of vanillymandelic acid to vanillin with molecular oxygen as the terminal oxidant for the first time. The effects of reaction conditions on the catalytic performances have been investigated in detail, almost 100 % conversion of vanillymandelic acid and 88.3 % yield of goal product were achieved under the best conditions of reaction time 6 h, oxygen pressure 0.45 MPa, 85 °C and pH 12.5. In addition, the mesoporous CuO revealed outstanding recyclability and exhibited several pivotal advantages, including mild reaction conditions, environmentally friendly oxidant, as well as greatly reduced the amount of catalyst. A plausible mechanism for the liquid-phase oxidation of vanillymandelic acid on CuO was proposed.

**Keywords** Catalytic oxidation · Vanillymandelic acid · Mesoporous · Vanillin

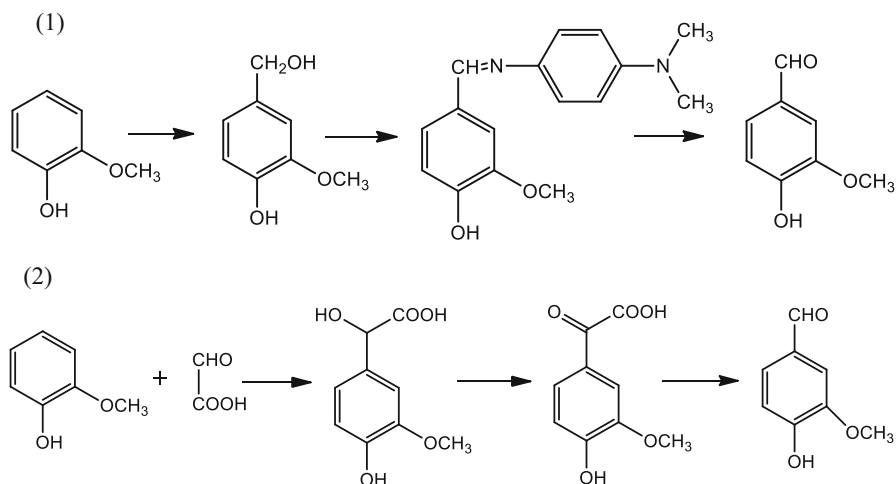
## Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is used worldwide as an edible flavor, it has a strong milk fragrant breath, used extensively in the food industry [1], pharmaceutical, nutrition [2], fine chemical industries [3]. Vanillin is one of the most popular flavoring materials and inspires a large number of researchers to find synthetic methods to prepare it [4]. The present industrial synthesis methods can be prepared from different materials, such as lignosulfonate [3, 5, 6], isoeugenol [7, 8], guaiacol [9], cresol [10], etc. In all these cases, the guaiacol route has become one of

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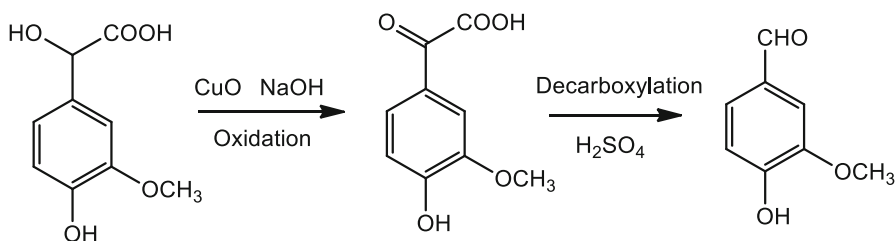
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**Scheme 1** Two different paths of the guaiacol route to synthesis vanillin

the most popular method in vanillin synthesis for its high efficiency, low pollution and simple implementation. It is well known that the guaiacol method includes two different paths (1) the nitrose method [11], (2) the glyoxylic acid method (Scheme 1) [9]. However, the complex separation manipulation, low yield, severe pollution make the nitrose method not an environmental friendly and economical path. On the other hand, the glyoxylic acid method is relatively simple and meets the demands for environmental friendliness. Traditionally, the guaiacol–glyoxylic acid method is composed of two continuous steps, including the condensation reaction and the oxidative decarboxylation of the intermediary vanillylmandelic acid (MHPA). An improved synthesis of the intermediary MHPA from the glyoxylic acid method has been reported by Niu et al. [12]. They found that MHPA can get the maximum yield of 88 % under the best conditions, which is more efficient than other previous studies. But due to the low yield of the oxidation reaction (Scheme 2), the synthesis of vanillin does still not meet the requirements. Thus, how to improve the oxidation reaction becomes critical for increasing the whole production rate. Based on existing research, another problem encountered in the oxidation reaction is that the homogeneous catalysts  $\text{CuSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$  were used in the oxidation process [13, 14], which does not only bring inconvenience in catalyst recycling but also causes difficulties in catalyst-product separation. Therefore, the use of homogeneous catalysts in industrial production is limited [15].

There are numerous reports on the improvement of the oxidation reaction using transition metal catalysts. Among them, copper-based heterogeneous catalysts show very interesting and promising catalytic activity. The oxidation reaction between MHPA and copper compounds (copper hydroxide,  $\text{CuO}$  nanocrystals), according to a previous report, was carried out under normal pressure, and fresh air was fed into the reactor throughout the whole process [16]. Such systems typically need high temperature, which not only contributes to low oxygenate yields, but also lead to the



**Scheme 2** Synthesis of vanillin by oxidation of vanillylmandelic acid and followed by a decarboxylation step

poor product purity, due to the further oxidation of product. Recently, You et al. reported that when the reaction pressure reach 0.9 MPa, the optimized molar ratio of MHPA: copper(II) is 1.5:1 [14]. Large amounts of catalyst are used in the reaction in order to obtain a high yield of vanillin, which could cause water pollution and waste of resources. Thus, it is of particular interest to know whether it is possible to get environmental friendly oxidation reaction and higher amounts of vanillin using the cheap CuO catalyst under mild conditions.

With this in mind, we report here that mesoporous CuO synthesized by hydrothermal method act as an effective heterogeneous catalyst for the oxidation of MHPA to vanillin with molecular oxygen as oxidant for the first time. In addition, the use of molecular oxygen is in line with the concept of green chemistry [17–19]. The reaction mechanism pathway for vanillin production from MHPA oxidation over CuO was discussed as well. In order to achieve good control effect, a systematic study concerning the oxidation reaction between MHPA and CuO has been discussed in depth. The influences of various factors on the reaction were optimized one after another to get a better understanding of how to control the reaction conditions.

## Experimental

### Preparation of CuO catalyst

The commercially available products were used without further purification. The preparation of the CuO catalyst was carried out by the following method. Briefly, a simple hydrothermal method was used to synthesize phase-pure CuO with Sierpinski-like structure. 3.993 g cupric acetate monohydrate ( $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ , Greagent) and 1 g NaOH (Greagent) were mixed with 40 mL of deionized water, and then stirred at 40 °C for 1 h. The mixture was transferred to a Teflon-lined stainless steel autoclave with 50 mL volume, then heated and kept at 140 °C for 12 h. The precipitate was collected by centrifugation after the autoclave was cooled down to room temperature, and washed with deionized water and absolute ethanol. Finally, the precipitation was dried under vacuum at 60 °C for 24 h.

## Catalyst characterization

X-ray diffraction patterns (XRD) were obtained with a Bruker D8 X-ray diffractometer using Cu  $K_{\alpha}$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ), operated at 40 kV and a current of 40 mA over the  $2\theta$  range of  $10\text{--}80^{\circ}$ . The catalyst morphology was observed through a scanning electron microscope (SEM, BRUKERS-3400N). Transmission electron microscopy (TEM) investigations were performed with an FEI Tecnai G2 20 microscope operated at 200 kV. BET surface areas and pore diameter distribution of the samples were measured according to the  $N_2$  adsorption isotherms measured by a Micrometrics ASAP 2010. The sample was degassed at 573 K and  $10^{-3}$  Pa for 10 h prior to the measurement, and the specific areas were calculated by the BET method. Pore size distribution (PSD) curves were derived from the Barrett–Joyner–Halenda (BJH) method using the adsorption branches. Raman spectra were obtained in a LabRAM Aramaic micro Raman spectrometer.

## Catalytic activity test

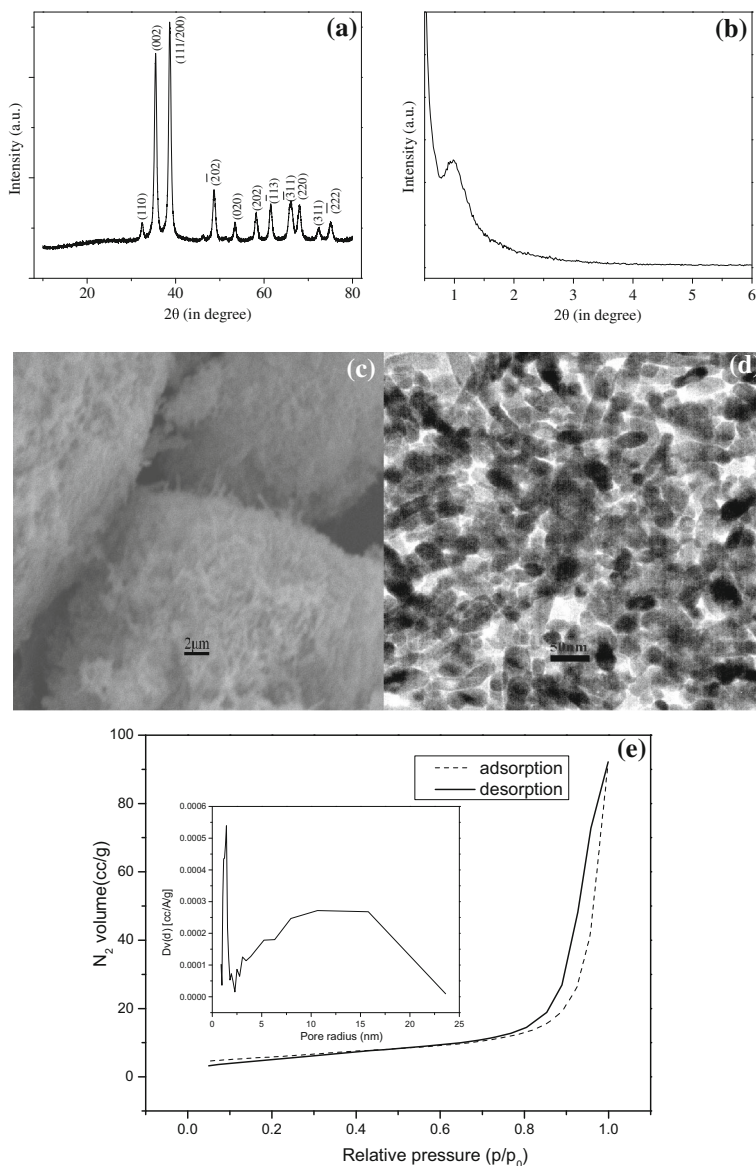
Vanillin was synthesized via the oxidative decarboxylation of MHPA. Typically, 0.5955 g MHPA (vanillylmandelic acid, Sigma Aldrich) 0.1 mol/L NaOH, and 0.046 g CuO were added into the high pressure reaction kettle successively. The pH of the reaction medium was 12.5 and after the reactor was charged with 0.45 MPa  $O_2$  at room temperature, the reaction was carried out at  $85^{\circ}\text{C}$  for 6 h with vigorous stirring. After the reaction finished, the reactor was cooled down to room temperature, the liquid products together with unreacted substrate were collected by removing the solid catalyst via centrifugation, and adjusted to pH 3 with 50 wt% sulfuric acid at  $40^{\circ}\text{C}$  for 2 h. The solution was heated to  $70^{\circ}\text{C}$  and kept at this temperature for 1 h in order to decarboxylate completely, then cooled down to room temperature. The solution was then extracted with ethyl acetate ( $4 \times 30$  mL), removing the solvent by vacuum distillation. Finally, the oxidative decarboxylation product was identified by  $^1\text{H}$ NMR and quantitated by HPLC.

The catalyst CuO was collected by centrifugation and washed with deionized water and absolute ethyl alcohol, then dried in air at  $100^{\circ}\text{C}$  for 3 h. The dried catalyst could be used in the recycling tests.

## Results and discussion

### Catalyst characterization

Fig. 1a shows the X-ray diffraction (XRD) pattern of the sample prepared at the reaction temperature  $140^{\circ}\text{C}$ . It can be seen that all the peaks correspond to the reflections from (110), (002), (111/200), ( $\bar{2}$ 02), (020), (202), ( $\bar{1}$ 13), ( $\bar{3}$ 11), (220), (311) and ( $\bar{2}$ 22) planes of monoclinic cupric oxide, which are consistent with the standard reported values (JCPDS File no. 41-0254). Fig. 1b gives the small-angle powder X-ray diffraction pattern of the final CuO sample. There is no distinctive



**Fig. 1** XRD patterns of the **a** Siberia-cocklebur-like structures CuO sample prepared at 140 °C for 12 h, **b** Small-angle powder X-ray diffraction pattern of the CuO sample prepared at 140 °C for 12 h. **c** SEM image of the CuO siberia cocklebur sample prepared at 140 °C for 12 h. **d** TEM image of mesoporous CuO sample. **e** N<sub>2</sub> adsorption/desorption isotherms of mesoporous CuO structures. The *inset* of **e** shows the pore radius distributions of CuO siberia cocklebur sample

higher-order diffraction observed and a single broad diffraction peak at low 2θ suggesting the disordered mesophases [20]. Fig. 1c shows the oval Siberia-cocklebur-like structures of the final product obtained at 140 °C for 12 h, and a lot

of fluffy needles can be seen on the solid surface. Fig. 1d displays the TEM image of the CuO with the siberia cocklebur structure, which also reveals that the siberia cocklebur structure was assembled by the CuO nanorods with an average length and diameter of 2.23 and 0.95 nm. Fig. 1e shows the N<sub>2</sub> adsorption/desorption isotherms of CuO samples at 77 K. These isotherms with a hysteresis loop in the relative pressure range of 0.4–1.0 can be classified as type IV. The BET surface area was found to be 20.6 m<sup>2</sup> g<sup>-1</sup>. The inset of the Fig. 1e gives the pore size distributions of the CuO siberia cocklebur structure, the isotherms bias x-axis and adsorption volume is small at low pressure and the type-IV isotherms indicates a mesoporous material. Moreover, according to the hysteresis loop, the mesoporous structure can be looked upon as slit hole which is formed by the accumulation of particles and in conformity with the TEM image.

### Reactivity of catalyst

The catalytic performance of the different catalysts in the oxidation of MHPA by molecular oxygen is listed in Table 1. Data were taken at the optimum experimental conditions, which were determined as described in the following sections. As shown in Table 1, using CuSO<sub>4</sub> and CuO nanocrystals as catalysts afforded 100 % conversions of MHPA, the yields of vanillin were 83.5 and 78.7 %. A great disadvantage is that CuSO<sub>4</sub> as an oxidation catalyst usually comes with complicated catalyst-product separation procedure and causes low-pure products. It is noteworthy that the as-prepared mesoporous CuO as heterogeneous catalyst avoid the shortcoming successfully, and give highly satisfactory yields of vanillin (Table 1, entry 3). A comparison of the CuO nanocrystals with the porous CuO shows that the latter favored the oxidation reaction, which will be used in the following step.

### Effects of reaction parameters on the oxidation of MHPA to vanillin

#### *Effect of reaction time*

The effects of reaction parameters including reaction time, reaction temperature, oxygen pressure, catalyst amount, and PH value on the MHPA oxidation were investigated. According to the previous studies, it is obvious that the reaction time is

**Table 1** The oxidation of MHPA with different catalysts

Entry	Catalyst	Time (h)	Conversion (%)	Sel (%)
1	CuSO <sub>4</sub>	6	100	83.5
2	CuO <sup>a</sup>	7	100	78.7
3	CuO <sup>b</sup>	6	100	88.3

Reaction conditions: temperature 85 °C, pH 12.5, 0.45 MPa O<sub>2</sub> pressure, CuO amount 0.046 g

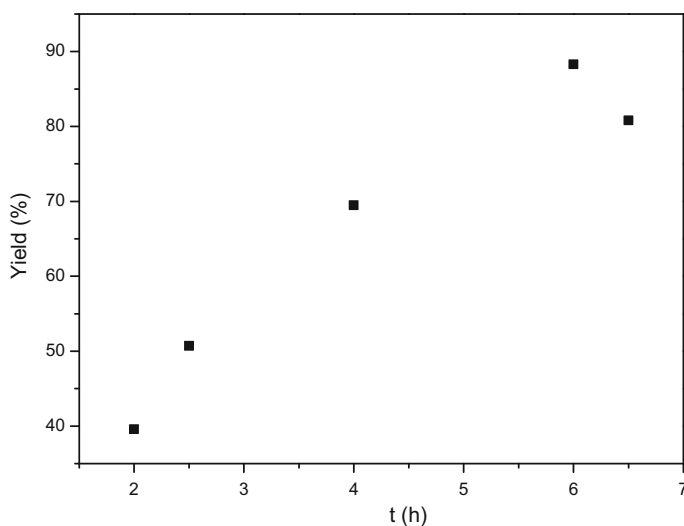
<sup>a</sup> CuO nanocrystals and the BET surface area was found to be 7.56 m<sup>2</sup>/g

<sup>b</sup> Mesoporous CuO

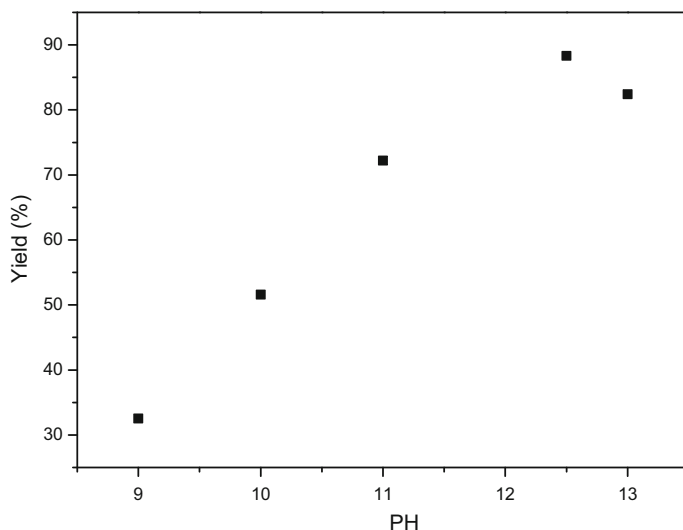
important for restraining the undesired reactions. Fig. 2 shows the dependence of the product yield on reaction time. The oxidation reaction was studied at the conditions of the reaction temperature 85 °C, oxygen pressure 0.45 MPa, pH 12.5, and catalyst amount 0.046 g. It was observed that increasing reaction time was favorable to the oxidation reaction, the yield of vanillin was pronouncedly enhanced to 88.3 % at 6 h, and prolonging reaction time to 6.5 h, the MHPA conversion approached 100 %, but the selectivity of vanillin decreased accompanied with the increase in the vanillic acid yield, probably due to the further oxidation of vanillin under the experimental conditions. The results show that it is necessary to maintain the reaction time at 6 h.

### *Effect of pH*

It has been confirmed that the pH of the reaction medium is crucial to the oxidation reaction. In the experimental process, large amounts of NaOH were used to protect the phenolic group and avoid the formation of polymers and tars [21]. Therefore, the reaction pH was adjusted to 9, 10, 11, 12.5, 13, and the results are shown in Fig. 3. It can be observed that the yield of vanillin is merely 32.5 %, which is due to the incomplete reaction at pH 9. Gradually adding NaOH solution to the reaction medium increases the yield linearly with the rising of pH value. A further increase to pH 12.5 brings the highest vanillin yield 88.3 %. But when the pH reaches 13, the yield of vanillin slightly declines. So, the high pH value does not only lead to lower yield of the desired product, but also wastes alkali liquor. Taking all of these factors into consideration, it is better to maintain the pH at 12.5.



**Fig. 2** The effect of reaction time on the yield of vanillin. Other reaction conditions: 85 °C, PH 12.5, CuO amount 0.046 g, 0.45 MPa O<sub>2</sub> pressure



**Fig. 3** The effect of pH on the yield of vanillin. Other reaction conditions: 85 °C, CuO amount 0.046 g, 0.45 MPa O<sub>2</sub> pressure, reaction time 6 h

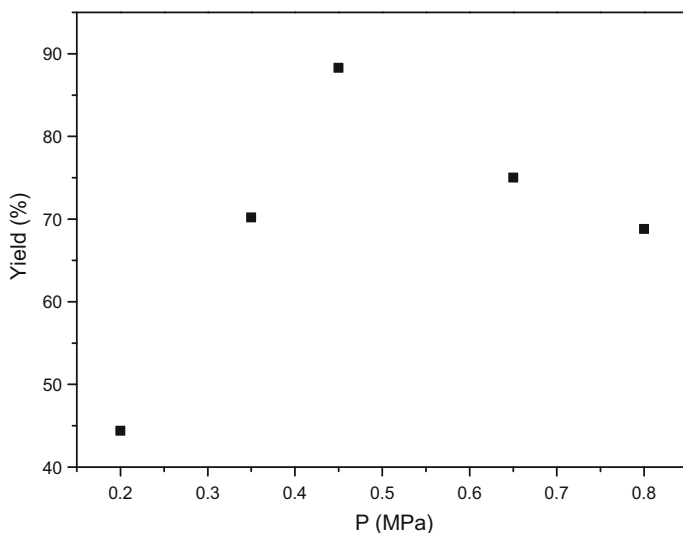
#### *Effect of oxygen pressure*

For an aerobic oxidation process, the oxygen pressure should be one of the most important factors for the oxidation result. The vanillin yield rose rapidly with oxygen pressure in the range of 0.2–0.45 MPa. At the relatively low O<sub>2</sub> pressure of 0.2 MPa, only a small amount of vanillin was obtained as shown in Fig. 4. However, upon increasing the O<sub>2</sub> pressure to 0.65 MPa, the MHPA conversion kept almost unchanged, while the vanillin yield tremendously declined, indicating overoxidation of goal product at higher O<sub>2</sub> pressure (Scheme 3). Therefore, proper oxygen pressure is necessary to the oxidation reaction. According to the results, appropriate O<sub>2</sub> pressure for the reaction should be 0.45 MPa.

#### *Effect of reaction temperature*

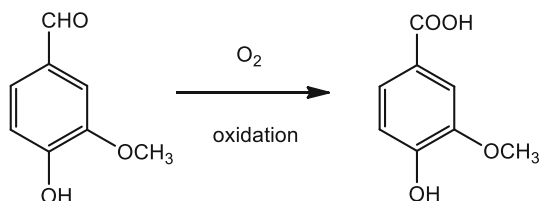
The reaction temperature apparently influences strongly the selective catalytic oxidation of MHPA to vanillin, it should be noticed that the elevated temperature will be undoubtedly helpful to accelerate the oxidation reaction, but the higher temperature will also lead to side reactions. As shown in Fig. 5, the yield of vanillin largely increased with increasing reaction temperature, indicating low temperature was unfavorable to the reaction. The yield has increased by 20 percent when the temperature increased from 65 to 75 °C, and increased from 80 to 88.3 % with the temperature from 75 to 85 °C. The red-brown byproduct caused by deep oxidation became conspicuous when the temperature mounting to 95 °C. Therefore, 85 °C was selected as the proper reaction temperature.





**Fig. 4** The effect of oxygen pressure on the yield of vanillin. Other reaction conditions: 85 °C, CuO amount 0.046 g, pH 12.5, reaction time 6 h

**Scheme 3** Overoxidation of goal product at higher O<sub>2</sub> pressure

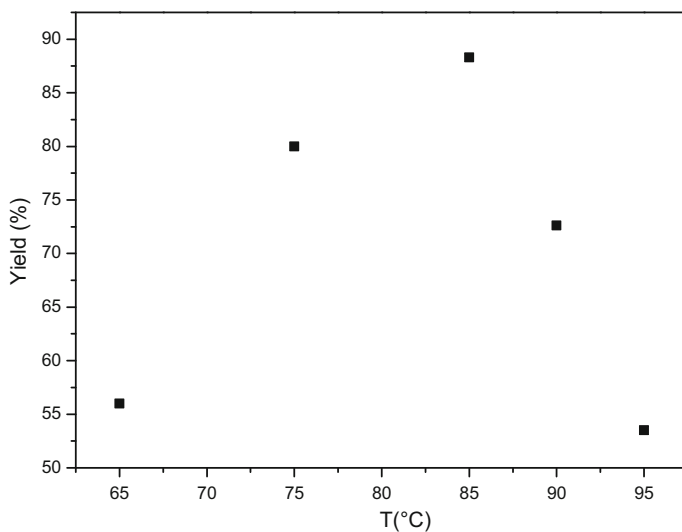


### *Effect of catalyst amount*

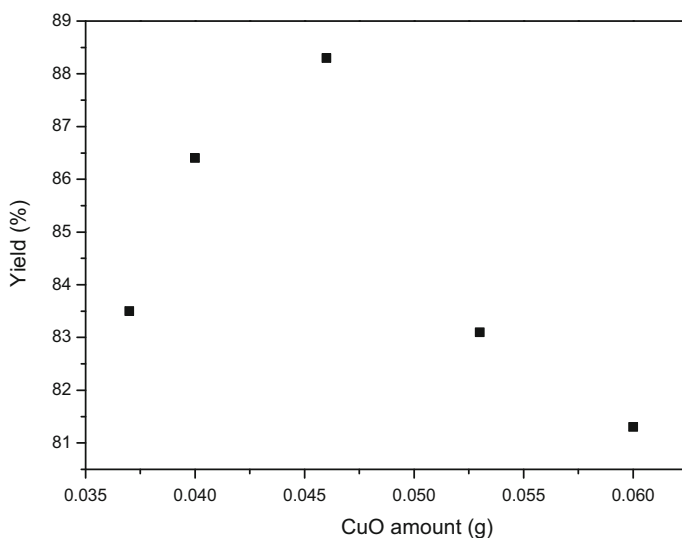
In order to restrain the undesired side reactions, we also studied the effect of the CuO amount on the yield of vanillin. The amount of MHPA was an invariable value throughout the process, herein 0.5955 g. As shown in Fig. 6, increasing the amount of CuO to 0.046 g rapidly improved MHPA conversion to 100 % and vanillin selectivity to 88.3 %, showing that the catalyst amount plays an important role in MHPA oxidation. Further increasing the amount of CuO to 0.06 g, the MHPA conversion did not change significantly, while the yield decreased, which was attributed to further oxidation of vanillin. Therefore, 0.046 g was thought to be the optimal catalyst amount.

### **Reusability of the catalyst**

Finally, the recyclability of the CuO catalyst was tested by performing successive reuses of the catalyst in the oxidation reaction and the results of the conversion,



**Fig. 5** The effect of reaction temperature on the yield of vanillin. Other reaction conditions: pH 12.5, reaction time 6 h, CuO amount 0.046 g, 0.45 MPa O<sub>2</sub> pressure



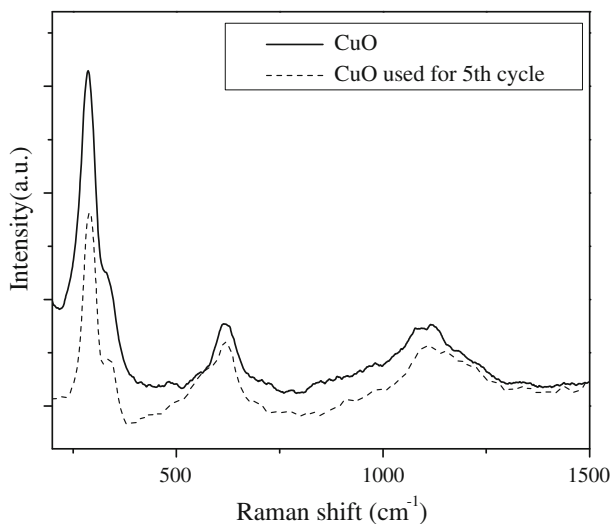
**Fig. 6** The effect of CuO amount on the yield of vanillin. Other reaction conditions: 85 °C, pH 12.5, reaction time 6 h, 0.45 MPa O<sub>2</sub> pressure

yield are displayed in Table 2. Obviously, the CuO catalyst can be recycled without a large loss in catalytic performance, and there is no difference in conversion during five cycling tests. Moreover, as can be observed in Fig. 7, compared to the pristine CuO, the Raman spectra of the used CuO was almost unchanged. Therefore, the

**Table 2** Recycling results of the mesoporous CuO for the oxidation of MHPA

Other reaction conditions:  
 temperature 85 °C, O<sub>2</sub> pressure  
 0.45 MPa, pH 12.5, CuO  
 amount 0.046 g

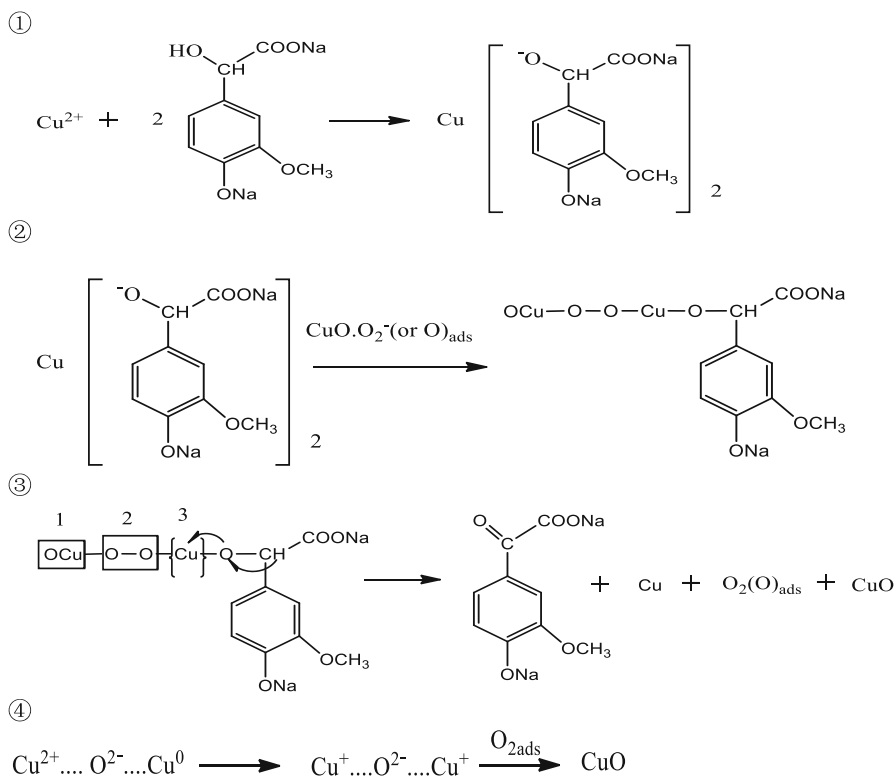
Cycle	Time (h)	Conversion (%)	Yield (%)
1	6	100	87.8
2	6	100	86.3
3	6	100	87.5
4	6	100	87.2
5	6	100	87.7


**Fig. 7** Raman spectra of pristine CuO and the used CuO

catalyst can be reused at least five times. This shows that CuO with a structure of siberia cocklebur has a commercial promise for industrial application in MHPA oxidation to vanillin.

### Mechanism of the oxidation reaction

It is generally accepted that mesoporous CuO is metal deficient ( $\text{Cu}_{1-\delta}\text{O}$ ) oxide material, surface defects of metal oxides act as O<sub>2</sub> adsorption sites, and then O<sub>2</sub> molecules adsorbed on the CuO surface capture the electrons [O<sub>2</sub>(gas) + e<sup>-</sup> → O<sub>2</sub>(adsorbed)] [20]. So, the radical nature of the unbound oxygen atom of the O<sub>2</sub> molecule is likely to be enhanced on account of O<sub>2</sub> adsorption on CuO surface [22], and then the peroxide-like CuO · O<sub>2</sub> (or O)<sub>ads</sub> compounds have been improved. Therefore, a plausible overall mechanism for this catalytic oxidation has been proposed (Scheme 4). The catalytic cycle begins by formation of the precursor perhydroxy-Cu<sup>2+</sup> complex (chemical equation ①, ②) [23], which has been considered to be an active species in many other catalytic reactions [24, 25], and then two electrons transfer from the precursor to Cu<sup>2+</sup> with concomitant



**Scheme 4** A plausible mechanism for the oxidation of MHPA catalyzed by CuO

reproduction of  $\text{O}_{2,\text{ads}}$  or  $\text{O}_{\text{ads}}$  species, and the oxidation product is formed at the same time (chemical equation ③) [26]. The reduction of CuO proceeds directly to Cu under these reaction conditions, in agreement with previous observations [27]. Then the transient  $\text{Cu}^0$  will be influenced by the neighboring oxygen ions, and by means of electron transfer formation of  $\text{Cu}^+ \dots \text{O}_2^- \dots \text{Cu}^+$ , copper valence of the catalytic surface cycles between II and 0 (chemical equation ④) [28].

## Conclusions

In conclusion, the present study reports a high-efficiency method for the oxidation of MHPA to vanillin with mesoporous CuO as the catalyst. The catalytic activity was higher than that of CuO nanocrystals catalyst under the same reaction conditions. Meanwhile, molecular oxygen was used as the terminal oxidant in accordance with the green chemistry, this approach makes the system a promising candidate for sustainable oxidation of MHPA to vanillin. Furthermore, it is worth mentioning that the CuO could be successfully re-used without significant loss in performance. In addition, we report a systematic study on the selective oxidation of

MHPA over mesoporous CuO for the first time. Under the best reaction conditions of reaction time 6 h, oxygen pressure 0.45 MPa, 85 °C and pH 12.5, we can get the maximum yield of 88.3 %. This will provide valuable data and theoretic contribution for the synthesis of vanillin.

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