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1 Introduction

As the major flavour component of vanilla beans, vanillin (3-methoxy-4-hydroxybenzaldehyde) is widely used in the food industry and perfumery due to its attractive aroma and favourable antioxidative effects.^{1–3} Thanks to its antimicrobial properties, vanillin is also used in the pharmaceutical industry as an important medical intermediate. Therefore, with the expansion of the application fields, the annual worldwide demand for vanillin has increased sharply.^{4,5}

At present, there are three sources for commercial vanillin: natural extraction, microbiological synthesis and chemical synthesis.⁶ Undoubtedly, the annual production of natural vanillin obviously cannot meet the annual global demand (about 1.5 million tons per year) due to the limited annual vanilla bean production and the vanillin content in the vanilla bean.^{7–9} The microbial fermentation method, plant cell culture

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An efficient environmentally friendly CuFe₂O₄/ SiO₂ catalyst for vanillyl mandelic acid oxidation in water under atmospheric pressure and a mechanism study[†]

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With the aim of the green production of vanillin, a highly efficient environmentally friendly oxidation system was introduced to oxidize vanillyl mandelic acid (VMA) with a porous $CuFe_2O_4/SiO_2$ component nano-catalyst in aqueous solution under atmospheric pressure. The N₂ adsorption–desorption pattern indicated that $CuFe_2O_4/SiO_2$ possessed a much higher specific surface area (49.98 m² g⁻¹) than that of $CuFe_2O_4$ (5.02 m² g⁻¹), which further indicated that the SiO₂ substrate restrained the aggregation of $CuFe_2O_4$ nanoparticles. The conversion for VMA and selectivity for vanillin reached 98% and 96%, respectively, under atmospheric pressure. The excellent catalytic performance was attributed to the synergistic effect of the catalytic capacity of $CuFe_2O_4$ and the adsorption capacity for the reactant of SiO₂. Simultaneously, the effect of different reaction conditions for catalyst activity and selectivity were investigated. Furthermore, the probable mechanism of VMA oxidation was investigated by *in situ* ATR-FTIR, H₂-TPR, XPS and ¹H NMR. More importantly, the decarboxylation was verified to proceed in basic conditions rather than in conventional acidic conditions.

method and enzymatic method supplied an efficient method for bio-vanillin production.¹⁰⁻¹³ The biosynthesis method satisfied consumers' desires for natural products and produced no by-product pollution for the environment. However, these methods have many disadvantages such as strict conditions for the microorganism's requirements, low yield, difficulties in production on a large-scale and so on. Simultaneously, using the biosynthesis method to produce vanillin results in a relatively high price. Conversely, chemically synthesized vanillin has the advantages of a wide range of raw materials, a simple synthesis process and being easily industrialized, which caused commercial vanillin to have a very cheap price compared with natural vanillin. The nitrification method, guaiacol-glyoxylic acid method, lignin/ syringaldehyde catalytic oxidation method, and organic electrochemical synthesis method are the typical chemical synthesis methods for vanillin production.¹⁴⁻¹⁸ However, the nitrification method and catalytic oxidation method face serious economic and environmental challenges due to high pollution, long processes and so on. Therefore, the guaiacol-glyoxylic acid method for vanillin production, which employs guaiacol and glyoxylic acid as raw materials was the most competitive method among the chemical methods due to the properties of low energy consumption, simple operation, environmentally friendliness and so on.

Generally, the guaiacol–glyoxylic acid method for vanillin production is divided into three processes.¹⁹ Firstly, the VMA is

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[†] Electronic supplementary information (ESI) available: HPLC spectra, IR spectra, ¹H NMR spectra and the stability of vanillin at different pH. See DOI: 10.1039/ d0nj04798h

produced under alkaline conditions (pH = 10-11) from guaiacol and glyoxylic acid condensation. Then, as an intermediate product in the reaction, VMA is used directly without separation from the reaction solution to produce 3-methoxy-4-hydroxy acetophenone under the oxidation of CoCl₂, bismuth (Bi²⁺ and Bi³⁺), reducible metal salts, copper hydroxide, copper sulphate and so on.^{20,21,41-43} Finally, 3-methoxy-4-hydroxy acetophenone is decarboxylated to give vanillin by adjusting the pH value to 3-4 using sulfuric acid. Undoubtedly, the oxidation of VMA is the key process to influence the vanillin yield. In industrial production, in which VMA oxidation is catalysed by 2-3 eq. CuO, there is the difficulty of catalyst recovery, regeneration and the high-cost materials of construction.²² Meanwhile, a yield of vanillin of only 88.3% is attributed to the low selectivity for vanillin under the catalysis of CuO, although the conversion of VMA reached nearly 100%. It is of great significance to improve clean manufacturing by using environmentally friendly catalysts to replace the heavily consumed CuO. The by-product in manufacturing was one of the main reasons for environmental pollution especially for some fine chemicals production. Thus, developing a highly efficient oxidation method is pivotal for VMA oxidation. Many researchers have developed strategies for VMA oxidation such as Cu-Al hydrotalcite catalyst, copper(11) complexes and so on. $^{\rm 23,24}$

However, many metal complex methods face difficulties in preparation and problems due to the inferior stability of the complexes. So, metal oxides, especially spinel transition metal oxides with the AB₂O₄ general type, such as CuFe₂O₄, MgAl₂O₄ and CoFe₂O₄ were widely used in super conductors, the magnetic core, humidity sensors and catalysis fields due to their possessing unique properties such as electronic, magnetic and optical properties.²⁵⁻²⁷ In the field of catalytic oxidation, CuFe₂O₄ has been widely used as a high efficiency catalyst because of its excellent catalytic activity, stable chemical properties and inexpensiveness.²⁸⁻³⁰ Due to the Jahn–Teller effect, the two crystal forms of CuFe₂O₄ (tetragonal and cubic), which are routed from the preparation and precursors have a pivotal role in the catalytic activities.31 Traditionally, CuFe2O4 nanoparticles catalysts can easily agglomerate during the calcination process. The agglomeration of the catalyst caused much CuFe2O4 cladding in the particles, which further decreases the catalytic activity. The agglomeration of the catalyst prevented the internal group contact with the substrate of the reaction which further reduced the catalytic efficiency.³² Employing a porous substrate to support the CuFe2O4 catalyst efficiently and thus further enhance the dispersity of the catalyst is a useful strategy for increasing the catalytic activity. The nano-SiO₂ substrate, as a typical porous material was introduced to increase the dispersity of CuFe₂O₄ because of its huge specific surface area, good stability, and inexpensive properties. Simultaneously, the porous SiO₂ was also helpful in enhancing the concentration of the reacting substrate due to the adsorption.

Hence, based on the persistent researching of vanillin production, a green catalytic system was designed to convert VMA to vanillin in aqueous solution under a low oxygen atmosphere by employing a high-efficiency silica supported copper ferrite (CuFe₂O₄/SiO₂) component catalyst. Compared with the 2.5 eq. (*vs.* VMA) chemical oxidizing agent requirement in vanillin industrial production, the catalytic system just needed 0.1 eq. (*vs.* VMA) CuFe₂O₄/SiO₂ catalyst to arrive at comparative conversion and selectivity. In addition, to explore the potential for industrial applications of the catalytic system, we also investigated the effects of pH value, oxygen partial pressure, reaction temperature and reaction time for the yield and selectivity of vanillin. Simultaneously, a probable mechanism for vanillin generation was proposed under *in situ* ATR-FTIR and ¹H NMR research. It provides theoretical guidance for vanillin catalytic production.

2. Experimental

2.1 Reagents and instruments

All materials were of AR grade. Guaiacol, glyoxylic acid (50% aqueous solution), tetraethyl orthosilicate (TEOS), absolute ethanol (EtOH, 99.5%), copper sulphate pentahydrate(CuSO₄· 5H₂O, 99.5%), iron chloride hexahydrate(FeCl₃·6H₂O, 99.5%), citric acid monohydrate (C₆H₈O₇·H₂O, 99%), ammonium hydroxide (NH₃·H₂O), sodium hydroxide (NaOH, 99%), hexadecyl trimethyl ammonium bromide (CTMAB), sulfuric acid (H₂SO₄, 99%), tetraethyl silicate (99%), acetonitrile, ethyl acetate (99%), and oxygen (99.99%) were purchased from Sinopharm Chemical Reagent Co., Ltd, China. All the mentioned chemicals were directly used without additional purification.

2.2 Experimental method

2.2.1 Preparation of the catalyst CuFe₂O₄/SiO₂. The coprecipitation method was implemented in the preparation of CuFe₂O₄.^{33,34} In a typical experiment, the procedure was as follows: CuSO4.5H2O (14.98 g, 0.06 mol) and FeSO4.6H2O (32.44 g, 0.12 mol) were dissolved into 300 mL of water by stirring. C₆H₈O₇·H₂O (37.83 g, 0.18 mol) was added into the mixture to dissolve the copper salt and iron salt completely. Ammonia water was added to adjust the pH value to 7. Then, the mixture was stirred at 100 °C for 3 h to obtain a colloid liquid. The colloid liquid was filtered under vacuum to give a bluish grey solid. The solid was calcined in a muffle furnace at 600 °C for 3 h. After cooling to room temperature, CuFe₂O₄ nanoparticles were collected with magnets. The freshly prepared CuFe₂O₄ nanoparticles were added to a 500 mL flask, followed by the addition of water (50 mL), ethanol (300 mL), CTMAB (10.0 g) and TEOS (35.0 g). After the addition of ammonia water (100 mL) at 45 °C dropwise, the reaction mixture was stirred for 6 h. The mixture was filtered after cooling to room temperature. The solid was washed with water and dried in vacuum at 45 °C. Finally, the solid was calcined at 600 °C for 5 h in a muffle furnace to obtain the CuFe2O4/SiO2 nanoparticles which was used for VMA oxidation directly.

2.2.2 Oxidation of VMA by CuFe₂O₄/SiO₂

Preparation of VMA. Guaiacol (62.07 g, 0.5 mol) and glyoxylic acid (62.19 g, 0.42 mol) were dissolved in deionized water (300 mL) under continuous stirring. The mixture was alkalized to pH = 11.5



Scheme 1 A schematic diagram of the synthesis of vanillin using glyoxylic acid.

using aqueous NaOH (1 M) and then kept at 20 °C for 24 h. After acidifying to pH = 4–5 with 1 M H₂SO₄, the excess guaiacol was recovered by extracting with EtOAc (150 mL \times 2). The aqueous solution was used for VMA oxidation directly without any further purification.

Scheme 1 and Scheme S1 (ESI[†]) show the vanillin preparation and the by-product generation, respectively. Freshly prepared catalyst (CuFe₂O₄/SiO₂ 1 g) was added to an aqueous solution of VMA (100 mL, 10%). The mixture was heated to 90 °C under constant stirring after the pH value was adjusted to 11 using aqueous NaOH (30%). Then, the mixture was bubbled with O₂ and stirred for 5 h. The high-performance liquid chromatography (HPLC) spectra of the reaction mixture before and after oxidation are shown in Fig. S1 (ESI[†]). After cooling down, the mixture was acidified using H₂SO₄ 10% to pH = 4 and extracted with toluene (60 mL) 3 times. The combined organic layers were dried over MgSO₄, filtered, concentrated and purified by silica-gel chromatography to give the purified vanillin. The IR and ¹H NMR spectra of vanillin are shown in Fig. S2 and S3 (ESI[†]).

2.2.3 Materials characterization. Scanning electron microscopy (SEM) was carried out on a Hitachi S-4800 transmission electron microscope. Transmission electron microscopy (TEM) was carried out on a Technai G2 20 TWIN. The X-ray powder diffraction (XRD) pattern was performed on a d/max-2200pc XRD diffractometer. The X-ray photoelectron spectroscopy (XPS) experiments were tested on a Thermo Escalab 250Xi system using Al-K α radiation ($h\nu$ = 1486.6 eV). The Brunauer-Emmett-Teller (BET) specific surface areas of typical products were performed at 77 K in a Micromeritics ASAP 2020 system.

¹H NMR spectra were obtained on a Bruker AVANCE III spectrometer operating at 500 MHz. The Raman spectra were recorded on Thermo DXR using a DPSS laser. *In situ* ATR-FTIR was measured on a Mettler Toledo Reactir-15. The H₂-TPR was performed by passing 10 vol% H₂/N₂ over 50 mg of catalyst at a heating rate of 5 °C min⁻¹. Prior to the measurement, the sample was pre-treated under argon atmosphere at 200 °C for 1 h, then the system was cooled to ambient temperature by purging with pure argon gas.

3. Result discussion

3.1 Characterization of the prepared $CuFe_2O_4/SiO_2$ composite catalyst

Field emission scanning electron microscopy (FESEM) was used to investigate the morphology of the CuFe₂O₄/SiO₂ composite catalyst. As shown in Fig. 1a, the morphology of the CuFe₂O₄ particles was an irregular powder with a size of 100-200 nm, which provides excellent conditions for the O2 and VMA adsorption. To further exhibit the dispersion of the CuFe₂O₄ nanoparticles on the SiO₂ powders, transmission electron microscopy (TEM) was employed to investigate the fine structure of the CuFe₂O₄/SiO₂ component catalyst. Fig. 1b indicates the CuFe₂O₄ nanoparticles with the size of 20-40 nm deposited on the surface of SiO₂ uniformly. Further details concerning CuFe₂O₄/SiO₂ were observed by HR-TEM. As shown in the HR-TEM image, average d-spacing values of 0.25 nm were observed clearly, which corresponded to the distance of the (311) crystal planes of CuFe₂O₄. The equal dispersion of CuFe₂O₄ nanoparticles on a SiO₂ porous substrate was beneficial to retain the activity of the CuFe₂O₄ nanoparticles for VMA oxidation by restraining its conglomeration. To better determine the CuFe₂O₄ loading on SiO₂ obtained, the CuFe₂O₄/SiO₂ was characterized by energy-dispersive spectroscopy (EDS). As shown in Fig. S4 (ESI⁺), the CuFe₂O₄ loading amount was 12.5%. To further examine the chemical elements and states of the designed catalyst, XPS analysis was applied to investigate the concentration and binding energy of the surface



Fig. 1 (a) A field emission scanning electron microscopy (FESEM) image of $CuFe_2O_4/SiO_2$ and (b) a transmission electron microscopy (TEM) image of $CuFe_2O_4/SiO_2$.



Fig. 2 (a) X-ray photoelectron spectroscopy (XPS) of CuFe₂O₄/SiO₂ and (b–d) high-resolution XPS spectra of Cu 2p, Fe 2p and O 1s.

atoms present in the CuFe₂O₄/SiO₂ component catalyst. The C 1s peak at 284.6 eV in the environment was used as a correction. In the survey spectrum in Fig. 2a, the elements of Si, Cu, Fe, and O can be observed clearly. The binding energy values of Fe 2p and Cu 2p for the sample were detected at 710.5 and 936.7 eV, respectively. The obtained results obviously implied that both iron ions and copper ions are present in CuFe₂O₄/SiO₂ powders. Fig. 2b showed the XPS spectra of Cu 2p in freshly prepared CuFe₂O₄ and CuFe₂O₄/SiO₂. The Cu 2p spectrum of fresh CuFe₂O₄ and CuFe₂O₄/SiO₂ overtly shows four peaks at 634.5 eV for Cu 2p_{3/2}, 654.5 eV for Cu 2p_{1/2}, 942.1 eV for the Cu 2p_{3/2} satellite feature and 962.1 eV for the Cu 2p_{1/2} satellite feature, which indicates that the catalyst contained only Cu(II).^{35,36} Generally, as for the Fe 2p core level peak, the XPS spectra of the Fe 2p regions can be fitted into three contributions (FeO, Fe₂O₃ and Fe_3O_4). XPS spectra of Fe 2p core level is resolved into four peaks at 709.6, 710.9, and 712.7 eV for Fe $2p_{3/2}$, 724.4 eV for Fe $2p_{1/2}$ and a satellite signal at 717.5 eV. For Fe $2p_{3/2}$, the peak at 709.6 eV is indexed to Fe(II), whereas the peaks at 710.9 and 712.7 eV are indexed to Fe(III).37 From the comparison of CuFe₂O₄ and CuFe₂O₄/SiO₂ in the XPS spectrum, the valence state of the metal elements had no obvious changes, which indicates that the CuFe2O4 is well maintained before and after loading on SiO₂. In addition, as shown in Fig. 2d, the shape of the wide and asymmetric peak of the O 1s spectrum indicates that there can be more than one chemical state according to the binding energy. The peaks centered at 529.4 eV, 531.5 eV and 533.4 eV belong to the metal oxides (O–Cu–O and O–Fe–O), surface hydroxyl groups (OH) and SiO₂, respectively.³⁸

The crystal structure of the catalyst was examined using X-ray diffraction pattern (XRD). As seen in Fig. 3a, the peaks at 18.30, 29.94, 35.4, 36.94, 43.28, 53.4, 57.0 and 62.5° can be ascribed to the reflection of (111), (220), (311), (222), (400), (422), (511) and (440) CuFe₂O₄. In the XRD spectrum of CuFe₂O₄/SiO₂, the position and relative intensity of the diffraction peaks were in accordance with those of CuFe₂O₄ no peaks of the other compounds were observed. In the CuFe₂O4/SiO₂ nanoparticle sample, there will be a broad peak at 22°, which indicates that the crystallinity of SiO₂ was reduced.³⁹⁻⁴¹

As a porous material, SiO₂ supplied an efficient adsorption site for the oxide reaction. Thus, SiO₂ supported CuFe₂O₄ can effectively increase the specific surface area of the catalyst and the contact area during the catalyst and the reactants, thus further improving the catalytic efficiency of the catalyst. As shown in Fig. 4, the surface area has dramatically increased after constructing CuFe₂O₄ nanoparticles on the surface of SiO₂. Additionally, with the CuFe₂O₄ loading on SiO₂ the surface area was progressively increased from 5.017 to 49.98 m² g⁻¹. The large specific surface area of CuFe₂O₄/SiO₂ can offer more adsorption and reaction sites, consequently leading to enhanced catalytic activity for VMA conversion.



Fig. 3 (a) X-ray diffraction (XRD) of CuFe₂O₄/SiO₂ and CuFe₂O₄ and (b) X-ray diffraction (XRD) of CuFe₂O₄/SiO₂ before and after using for 5 cycles.



Fig. 4 The multilayer adsorption–desorption curve (BET) diagram of CuFe_2O_4/ SiO_2 and CuFe_2O_4.

3.2 The $CuFe_2O_4/SiO_2$ promoted highly efficient vanillin production

Due to the synergistic effect of the $CuFe_2O_4$ nanoparticles and SiO_2 substrate, the $CuFe_2O_4/SiO_2$ component catalyst showed excellent activity for VMA conversion. As exhibited in Fig. S1 (ESI†), only vanillin was detected by HPLC after 3 hours of stirring, which indicated that the catalyst possesses excellent selectivity for vanillin. Simultaneously, to evaluate the application prospects of the catalyst, various parameters such as the effect of SiO₂ substrate, pH value, catalyst loading and so on for vanillin production and VMA conversion were investigated. As a porous substrate, the SiO₂ supplied a useful substrate for O₂ and VMA adsorption, which further promoted the conversion of VMA. As shown in Table 1, the $CuFe_2O_4$ catalyst without loading on the SiO₂ substrate showed 83.7% VMA conversion, while the value in the $CuFe_2O_4/SiO_2$ system was 98.1%, which

Table 1 A comparison of the catalytic effect of $\mbox{CuFe}_2\mbox{O}_4/\mbox{SiO}_2$ with different catalytical systems

Catalyst	VMA conversion (%)	Vanillin selectivity (%)	Vanillin yield (%)
CuFe ₂ O ₄	83.7	96.7	80.9
CuFe ₂ O ₄ /SiO ₂	98.1	96.5	94.7
CuSO ₄	100	81.1	88.1
CuO ²²	100	88.3	88.3
$Cu(OH)_2^{42}$	_	_	56
$Bi(0)^{43}$	97	87	84.4
CoCl ₂ ⁴⁴	100	85	85

The reaction conditions as follows: reaction temperature: 90 $^{\circ}$ C, O₂ pressure: 0.1 MPa, pH value: 11.0, reaction time: 3 h, catalyst ratio: 10% *vs.* the amount of VMA.

further indicated the high efficiency of $\text{CuFe}_2\text{O}_4/\text{SiO}_2$. The selectivity for vanillin of the two catalysts was 96.7% and 96.5%, respectively, which indicated that the SiO_2 substrate had no obvious restrain for vanillin selectivity. As the optimal process in the vanillin industry at present, CuO showed 100% conversion VMA and 88.3% selectivity for vanillin.²¹ However, it was noted that the CuO requirement was more than 2.5 eq. (*vs.* VMA) to ensure VMA conversion. Such a CuO amount used caused the difficulties of vanillin purification, the high cost of oxidation agent regeneration, the waste of resources and so on.

The pH value of reaction mixture was investigated without any changes made to the other conditions. The pH value of the reaction system was about 4–5 after the recycling of the redundant guaiacol. The influence of the pH value changing from 4 to 12.5 was investigated. As shown in Fig. 5a, after the pH value was adjusted to 8, the yield of vanillin raised sharply. Following the constant rising of the pH value, the yield of vanillin increased accordingly. The vanillin yield reached 93.2% at a pH value of 11.0. However, the yield and conversion of vanillin declined as the pH value continued to increase. The reason might be attributed to the poor stability of vanillin in the high alkali environment. Thus, the stability of vanillin



Fig. 5 (a) The effect of pH on the yield and conversion of vanillin; (b) the effect of time on the yield and conversion of vanillin; (c) the effect of temperature on the yield and conversion of vanillin; (d) the effect of pressure on the yield and conversion of vanillin; (e) the effect of $CuFe_2O_4$ loading amount on the yield and conversion of vanillin; and (f) the effect of catalyst amount on the yield and selectivity of vanillin.

under different pH values was introduced to verify the assumption. As shown in Fig. S5 (ESI[†]), the vanillin content was decreased persistently following the pH value increase. Especially, the vanillin content showed a sharp decrease as the pH value exceeded 12. Because of the activity of the aldehyde compound between alcohol and acid, the reaction time and temperature will be important factors for the yield and selectivity of vanillin during industrial processes in the future. Therefore, the effect of reaction time for vanillin production was investigated with the other conditions unchanged. Experimental results indicated that the conversion of VMA was decreased following the reaction time and temperature increasing (>3 h, >95 °C). Simultaneously, the vanillin production increased persistently following the reaction time and temperature increase (<3 h, <95 °C). As shown in Fig. 5b, the yields for vanillin and conversion for VMA were 66.7% and 69.6%, respectively, after stirring at 90 °C for 1 h. As the reaction lasted for 3 h, the yield of vanillin reached 93.1% with the conversion of VMA at 98.3%. It indicated that the VMA conversion increased continuously with high selectivity following the reaction time in the first 3 h. As the reaction lasted for 5 h, the vanillin yield decreased to only 53.6% with the VMA conversion remaining at 98.4%. The dominant by-product of the oxidation was vanillic acid which was produced by over oxidation of vanillin. HPLC also indicated that vanillic acid increased obviously as the vanillin deceased. As the overall yield of vanillin decreasing was attributed to the selectivity of vanillin reducing after 3 h, the reaction should be terminated after 3 h. The effect of reaction temperature on the vanillin production was investigated with the other conditions kept the same.

As shown in Fig. 5c, the conversion of vanillin reached 57.2% at 70 $^{\circ}$ C and the yield of vanillin was only 56.1% due to the low conversion of VMA. When the temperature exceeded 90 $^{\circ}$ C, the vanillin produced in the reaction system was converted into vanillic acid, which reduced the selectivity of vanillin. The results showed that the highest yield of vanillin was obtained at 90 $^{\circ}$ C with the values of the yield and the conversion being 92.9% and 97.8%, respectively.

Due to vanillin being a widely used food additive added to food directly, developing a suitable oxidant is vital to convert VMA to vanillin. Oxygen is preferred because of its inherently inexpensive, clean and nontoxic properties. Undoubtedly, a higher O2 pressure has greater safety risks for the oxidation reaction. Meanwhile, vanillin will be easily oxidized to vanillic acid in the VMA oxidation process under a high oxygen pressure. The effect of oxygen partial pressure during vanillin production was investigated to determine the suitable O₂ pressure with the other conditions unchanged. As shown in Fig. 5d, the VMA conversion and vanillin selectivity decreased rapidly following the increasing of O_2 pressure. As the oxygen pressure increased to 0.2 MPa from 0.1 MPa, the yield of vanillin decreased to 77.5% from 92.9% with the conversion increasing to 97.1% from 98.4%. The primary by-product was vanillic acid which was produced by the high O2 pressure. Following reduction to 43% under 0.5 MPa O_2 pressure. As a result, the oxygen partial pressure plays a decisive role in the vanillin generation. Exorbitant O₂ pressure caused the generation of vanillic acid which decreased the yield of vanillin. The loading amount of CuFe₂O₄ in the catalyst of CuFe₂O₄/SiO₂ was one of the vital factors affecting the yield of vanillin. Therefore, the catalytic

effect of the catalyst under different CuFe₂O₄ loading amounts was investigated with the other conditions unchanged. As shown in Fig. 5e, VMA conversion increased from 47.1% to 96.4% following the CuFe₂O₄ loading amount added increasing from 2.5% to 12.5%. Simultaneously, the yield of vanillin increased from 45.2% to 92.5%. Furthermore, the yield for vanillin had no further changes as the CuFe2O4 loading amount over 12.5%. The ratio (vs. VMA) of CuFe₂O₄/SiO₂ used significantly affects the catalytic efficiency of the reaction. Thus, the influence of CuFe₂O₄/SiO₂ ratio (vs. VMA) using for VMA conversion and vanillin production was investigated with the other conditions unchanged (the reaction mixture was stirred at 90 °C for 3 h under the oxygen partial pressure of 0.1 MPa). Fig. 5f exhibited the VMA conversion and vanillin selectivity following the CuFe₂O₄/SiO₂ ratio varying from 0% to 20%. As the catalyst ratio increased to 10% from 0, the catalytic efficiency of the reaction increased from 9.8% to 93.4% accordingly. As the catalyst ratio further increased over 10%, the catalytic efficiency showed no obvious changes, and the oxidation efficiency stabilized at about 93.5%. A recycling experiment of CuFe₂O₄/SiO₂ for VMA oxidation was investigated to examine the stability of the catalyst, thus further evaluating the industrial production prospects. Thanks to the synergistic effect of $Cu(\pi)/Cu(1)$ and $Fe(\pi)/Fe(\pi)$, the catalyst was equipped with excellent catalytic stability for VMA oxidation. The VMA conversion, vanillin yield and selectivity corresponding to the CuFe₂O₄/SiO₂ reusing times are summarized in Fig. 6a. Furthermore, the IR spectrum showed that the combined catalyst was stable after cycling for five times. Simultaneously, as shown in the XRD spectrum of CuFe₂O₄/SiO₂ after using it for five cycles (Fig. 3b), all the typical diffraction peaks were observed on the used catalyst, indicating the high stability of the catalyst. Furthermore, trace amounts of CuO were also observed on the XRD spectrum of the used CuFe₂O₄/SiO₂, indicating the partial decomposition of CuFe₂O₄/SiO₂. However, the partial decomposition of CuFe₂O₄/SiO₂ had no obvious impact on the catalytic activity compared with the fresh CuFe₂O₄/SiO₂.

3.4 Probable mechanism for vanillin production

In order to explain the mechanism of VMA oxidation, the reaction was investigated by employing in situ ATR-FTIR. The IR spectra of vanillin and VMA in water were collected from a series of undersaturated solutions with known solute concentrations. As the ability of CuFe₂O₄/SiO₂ to function as a VMA oxidation catalyst was established, the IR spectrum was employed to detect any of the likely intermediates by examining the evolution of the wavenumber in the range of 300-900 cm⁻¹ as a function of reaction time.45-47 To exhibit the reaction clearly, the differential absorption (ΔA) data was collected and processed as shown in Fig. 7a. Peaks pointing down indicate bands disappearing while those pointing up correspond to new bands appearing due to the catalytic reaction. The increased intensity of the ΔA value at 1633 cm⁻¹ vested to the band of C=O stretching vibration, which was attributed to the generation of intermediate ketonic acid by oxidation of benzyl alcohol in VMA.⁴⁸ At the same time, the increased peaks of ΔA at 1305 and 1107 cm⁻¹ belong to the C-C stretching vibration and conjugation of aromatic ketones following the intermediate ketonic acid generation. The peak at 786 cm⁻¹ might be due to the C-C stretching vibration. The decline of the peaks could be attributed to the fracture of the C-C bond caused by the decarboxylation of intermediate ketonic acid.⁴⁹⁻⁵¹ The further evolution of the ΔA spectra for VMA oxidation is seen more clearly in Fig. 7b, in which the peaks at 1633 cm^{-1} (intermediate ketonic acid), 1305 and 1107 cm⁻¹ (aromatic ketones) and 786 cm^{-1} (decarboxylation) were plotted *versus* reaction time. Therefore, as indicated in Scheme 2, a probable reaction pathway was proposed based on the in situ ATR-FTIR result.^{52,53} Thanks to the alkaline conditions and oxygen vacancies, VMA was adsorbed on the surface of the catalyst to ensure the efficient contact between VMA and the catalyst. Then, the Cu(II) ion in the catalyst was converted to Cu(I) as soon as the electrons of VMA transferred to the catalyst, accomplishing the pivotal intermediate (a-keto carboxylate radical) formation. Vanillin was



Fig. 6 (a) The stability of CuFe₂O₄/SiO₂ under 5 times recycling; and (b) the IR spectrum of CuFe₂O₄/SiO₂ after being recycled five times.



Fig. 7 (a) The oxidation of VMA under in situ ATR-FTIR. (b) Absorbance versus time for selected wavenumber under in situ ATR-FTIR for VMA oxidation.



Scheme 2 A probable mechanism for oxidative decarboxylation of VMA over $CuFe_2O_4/SiO_2$.

generated following the decarboxylation of the pivotal intermediate. Simultaneously, the catalyst was reborn under the presence of O_2 .

To further investigate the oxidation process, H₂-temperature programmed reduction (H₂-TPR) and XPS were employed to reveal the reduction states of the CuFe₂O₄/SiO₂ catalyst. As a combined redox catalyst, CuFe₂O₄ was the catalytic centre which was surrounded by SiO₂ substrate. After calcination at 600 °C for 5 hours, the redox sites formed due to the oxygen vacancies. The synergistic effects of CuFe₂O₄, CuO and Fe₂O₃ on the reduction behaviours were widely accepted.^{54–56} As shown in Fig. S6 (ESI†), the pure CuO had a strong peak at approximately 350 °C, corresponding to the reduction of Cu(n) to Cu(0). Compared with CuO and Fe₂O₃, the reduction site in the CuFe₂O₄/SiO₂ samples could be clearly discovered to shift to

the lower temperature region direction, demonstrating the synergy effect in CuFe₂O₄. The reduction sites of CuFe₂O₄/ SiO₂ indicated that CuO was reduced first, hence the Cu ions exhibited more active oxidizing properties when oxidizing VMA by using CuFe₂O₄/SiO₂.^{57,58} XPS was employed to investigate the element valence change of the catalyst before and after being used once. The XPS spectra indicated that the surface of CuFe₂O₄/SiO₂ was equipped with a high density content of Cu(II) and Fe(III), which further enhanced the catalytic activity by the convenient charge transfer between Cu(II)/Cu(I) and Fe(III)/Fe(II). As shown in Fig. 8(a), two new peaks appeared at 933.2 eV and 936.8 eV indexed to Cu(1) and Cu(11) in the used CuFe₂O₄/SiO₂. The generation of Cu(1) indicated the catalytic performance of the CuFe₂O₄/SiO₂ catalyst.⁵⁹⁻⁶² The generated Cu(I) was re-oxidized to Cu(II) under the presence of Fe(III). As in Fig. 8(b), similar with the fresh prepared CuFe₂O₄, the XPS spectrum for Fe 2p after being used 5 times was also resolved into five peaks at 709.6, 710.9, 712.7, 717.5 and 724 eV, corresponding to Fe(III) and Fe(IIII). In addition, a change in the Fe 2p spectrum in the fresh and spent catalysts was found, and two peaks at 709.6 eV and 712.7 eV could be identified as $Fe(\pi)$ and $Fe(\pi)$, respectively. The changes were attributed to the conversion of Fe(m) to Fe(m) accompanied by the change of Cu(n)to Cu(II). Simultaneously, little Cu(II) existed in the form of CuO which was in accordance with the peaks in the XRD at 38.8 and 48.7° (as shown in Fig. 3b).^{63,64} Small amounts of CuO formed on the surface of the catalyst after being used 5 times but the main component showed no obvious changes. As shown in Fig. 8(c), the XPS spectra of O 1s indicated that the valence state of O before and after use showed no significant change.

Furthermore, it was interesting to note that the decarboxylation proceeded under alkaline conditions rather than under acidic conditions. The traditional view for vanillin production was the decarboxylation of the α -keto carboxylate radical under acidic conditions. As soon as the reaction completed, the ¹H NMR spectrum of the reaction mixture indicated that the aldehyde group appeared at the chemical shift of 9.25 ppm



Fig. 8 High-resolution Cu 2p (a), Fe 2p (b), O 1s (c) XPS peaks of $\rm CuFe_2O_4/SiO_2$ before and after.

(as shown in Fig. 9 and Fig. S7, ESI†). The ¹H NMR spectrum of the mixture compared with that of vanillin in different solutions and pH values further indicated the H at 9.25 ppm, which is attributed to the aldehyde group generated from the decarboxylation under basic conditions. As a result, vanillin was finally generated after decarboxylation of the α -keto carboxylate radical in basic conditions rather than acidic conditions. Furthermore, the loading of CuFe₂O₄ on the SiO₂ substrate provided efficient adsorption sites for oxygen molecules and favourable conditions for decarboxylation due to the large surface area.³²



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Fig. 9 The aldehyde group H in ¹H NMR spectrum of the reaction mixture compared with that of vanillin in different solutions and pH values.

4. Conclusions

In summary, a SiO₂ supported CuFe₂O₄ composite catalyst was designed and prepared for vanillin high efficiency generation under low pressure in aqueous solution. The poly-porous structure of the composite catalyst was beneficial for O2 VMA adsorption which further causes the VMA oxidation at low O2 pressure (0.1 MPa). From the study on the condensation reaction, the results show that the conversion of VMA and the yield of vanillin were affected by the pH value, reaction time, catalyst amount, partial pressure of oxygen, and reaction temperature. Under the optimum conditions, the selectivity for vanillin and the yield of vanillin can reached 98% and 93%. The catalytic oxidation process used CuFe2O4/SiO2 catalyst to avoid the use of large amounts of CuO, and the catalyst can be easily recovered during magnetism of CuFe₂O₄/SiO₂. More importantly, the probable mechanism of the CuFe₂O₄/SiO₂ catalysed VMA oxidation was introduced by in situ ATR-FTIR, H2-TPR and NMR. It provided new insights for the green oxidation of vanillyl mandelic acid.

Conflicts of interest

There are no conflicts to declare.

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