One-Pot Efficient Catalytic Oxidation for Bio-Vanillin Preparation and Carbon Isotope Analysis

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ABSTRACT: Vanillin (4-hydroxy-3-methoxybenzaldehyde) is one of the most widely used food spices. Aimed at bio-vanillin green production, the natural materials were directly catalytically oxidized efficiently in one pot under low O₂ pressure (0.035 MPa) in the presence of a non-noble metal oxidation combined catalyst (NiCo₂O₄/SiO₂ nanoparticles), which showed remarkable advantages of a short synthetic route and less industrial waste. The catalytic system showed good universality to many natural substrates with nearly 100% conversion and 86.3% bio-vanillin yield. More importantly, carbon isotope ratio investigations were employed to verify the origin of the organic matter. One hundred percent 14C content of the obtained vanillin was detected, which indicated that it was an efficient method to distinguish the vanillin from biomass or fossil materials. Furthermore, the 13C isotope examination showed effective distinguishing ability for the vanillin from a particular biomass source. The C isotope detection provides an effective method for commercial vanillin identification.

1. INTRODUCTION

The food quality and taste were attracting the attention of consumers following the social development. To improve the food taste, spices played a vital role attributed to their special aroma. In recent decades, more and more spices were developed as an important raw material in detergents, cosmetics, pharmaceuticals, fine chemicals industries, and biomass energy due to the aldehyde group and phenolic hydroxyl group. By addition, previous studies suggested that the natural spices also exhibited pharmacological effects via their anti-inflammatory activities and neuroprotective effects in vivo. As a typical representative, vanillin was the first synthetic spice used directly as a food additive to enrich food flavor (such as beverages, milk powders, confectionery, and so on) attributed to its pleasant smell. Simultaneously, vanillin prevented chemotherapy-induced kidney damage in rats by inhibiting inflammation, oxidative stress, and apoptosis. Due to the constantly expanding application field of spices, the global market requirement for spices had a large increase in the past decades.

At present, three types of vanillin (natural vanillin, bio-vanillin, and synthetic vanillin) were obtained due to the different materials for vanillin production attributed to the rapid development of science and technology. The primal vanillin, which is called natural vanillin, was extracted from vanilla bean initially. Undoubtedly, the natural spices extracted from plants were favorable in the premium food industry to improve the sweetness due to their composite fragrance. But the annual demand for vanillin was surpassing 1.75 × 10⁴ tons and the requirement increased constantly, while the annual output of dry vanilla beans for vanillin extraction was merely 2000 tons. Besides, the useful ingredients of spices in relevant plants were present at a much lower level, e.g., about 2–3% (w/w) vanillin in dry cured beans. Considering the slow growth of vanilla plants and the quite expensive extraction process, the synthetic way has been exploited as the main vanillin source (principally from lignin and guaiacol). Compared with natural vanillin, synthetic vanillin possesses higher purity attributed to the advanced industrial technologies. However, the fragrance of natural vanillin from vanilla was more pleasant than that of synthetic vanillin from fossil fuel because of the pleasant aroma caused by various natural ingredients’ flavor. Therefore, a large amount of “fake natural vanillin”, which is mixed synthetic vanillin, existed in the market for a much higher price (as shown in Table S1). The constantly increasing requirement for natural spice extracts has encouraged researching interests for new sources to obtain vanillin. Furthermore, the high production cost, tedious reaction steps (including the preparation of guaiacol), cumbrous separations, and vast amount of wastewater have brought heavy burdens for its mass manufacture in the face of the worldwide growing demand for vanillin.

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A sustainable approach to vanillin production is needed to be developed for the sake of economic interests, environmental considerations, industry, and so on over recent decades. One-pot chemical synthesis of bio-vanillin from natural materials can be considered as a potential process for the supplement of natural vanillin. Bio-vanillin was more competitive than fossil material-synthesized vanillin owing to its similar fragrance with natural vanillin. Different from fossil fuel-produced vanillin, bio-vanillin produced from natural materials by one-step oxidation possessed the advantages such as wide raw material sources, shorter synthetic steps, less industrial pollution, and so on. Therefore, one-pot oxidation prepares bio-vanillin from biobased 4-substituted guaiacol (such as 4-methyl guaiacol, ferulic acid, and eugenol), and lignin and other natural products will have an important significance in theory research. Natural materials were from a series of renewable energy sources with abundant reserves, low cost, and easy access, it attracted wide attention as clean energy and a chemical raw material. Especially, for some waste such as lignin, which has a similar structural unit with a guaiac base (the structure is shown in Figure S1, Supporting Information), converting it into vanillin has an important potential application value both in environmental and energy fields.

An efficient catalyst was a prerequisite to convert a bio-material to bio-vanillin. Owing to their low price, abundance, and environmental friendliness, transition-metal oxides, such as CuO, MnO2, Co3O4, CoMn2O4, and NiCo2O4, have caused considerable interest for selective oxidation. Among them, some mixed-valence metal oxides (e.g., NiCo2O4) were widely considered as a promising alternative to noble metal catalysts due to the versatile redox couples of Co3+/Co2+ and Ni3+/Ni2+. But the aggregation of NiCo2O4 nanoparticles was the prominent inhibiting effect for its catalytic activity. Loading the nanoparticles on the porous substrate was an effective strategy to overcome the agglomeration. Simultaneously, the low-cost porous substrate (such as SiO2) can also supply a sufficient specific surface area for reactant adsorption. Hence, NiCo2O4/SiO2 was constructed to convert bio-materials to bio-vanillin.

However, the synthetic bio-vanillin had the same properties (e.g., color, status, and so on) with those of natural vanillin and synthetic vanillin. But the natural vanillin was much expensive than the other types of vanillin due to its characteristic aroma. Hence, it is rather important to investigate an effective way to identify the sources of the three types of vanillin. The determination of stable isotope ratio mass spectrometry of carbon is presently a useful method for discrimination between natural vanillin, synthetic vanillin, and bio-vanillin. In the nature field, the 14C isotope is the radioactive C isotope among the multifarious carbon isotopes. Interestingly, the 14C content was the highest in living plants and animals and decreased after plants and animals died. Thus, the 14C isotope was widely used in paleoceanography, paleogeology, paleoclimatology, and so on to determine the geologic age. In addition, radiocarbon determination can well distinguish the petrochemical precursors from botanical precursors. With the 13C isotope as the stable carbon isotope, the ratio was not changed following temporal variation. The 13C isotope ratio (δ13C, isotope ratio of 13C/12C) of specific compounds can be affected by the biogenetic pathway (C3, C4, or CAM) and by environmental factors.

Herein, this work reported a low-cost NiCo2O4/SiO2 catalyst to oxidize a variety of typical natural precursors to vanillin by the one-step synthesis method under lower oxygen pressure (0.035 MPa). The catalytic system showed excellent performance in transferring various 4-substituted guaiacols (such as 2-methoxy-4-methylphenol) to vanillin with the separation yield of more than 86.3%. Simultaneously, the 14C and 13C isotopes of natural vanillin, bio-vanillin, and fossil material-synthesized vanillin were detected. Both the 14C ratios of natural vanillin and bio-vanillin were 100%, while that in fossil material-synthesized vanillin is 0%, which indicate that natural vanillin and bio-vanillin were from botanical precursors. The δ13C value of vanillin from different sources was varied, which indicates the biogenetic diverse pathway of botanical.

Figure 1. Field-emission scanning electron microscopy (SEM) sketch of (a) NiCo2O4 and (b) NiCo2O4/SiO2. Transmission electron microscopy (TEM) sketch of (c) NiCo2O4 and (d) NiCo2O4/SiO2.
precursors. This work provides a reliable basis for the identification of vanillin.

2. RESULTS AND DISCUSSION

2.1. Characterization Studies. The characterization of NiCo$_2$O$_4$/SiO$_2$ combined catalyst was investigated to reveal its excellent catalytic activity. To exhibit the dispersion of NiCo$_2$O$_4$ nanoparticles on SiO$_2$ powders, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to investigate the fine structure of the NiCo$_2$O$_4$/SiO$_2$ component catalyst. As shown in Figure 1a, the SEM image of NiCo$_2$O$_4$ without being loaded on SiO$_2$ showed a highly porous nanoflower cluster morphology. The TEM image indicated that NiCo$_2$O$_4$ has a thin sheet structure with a size of 40−100 nm (Figure 1b). After being loaded on SiO$_2$, significant aggregates were observed throughout NiCo$_2$O$_4$/SiO$_2$, but obvious pore structures will appear between the catalysts, which provide excellent conditions for O$_2$ and substrate adsorption (Figure 1c). As shown in Figure 1d, the NiCo$_2$O$_4$ nanoparticles with the size of around 50 nm were deposited on the surface of SiO$_2$ uniformly, and there is equal dispersion of NiCo$_2$O$_4$ nanoparticles on the SiO$_2$ porous substrate. To better determine the catalyst loading on SiO$_2$, energy-dispersive spectroscopy was used to test the combined elements of the NiCo$_2$O$_4$/SiO$_2$ component catalyst (as shown in Figure S2, Supporting Information).

X-ray diffraction (XRD) analysis was also performed to identify the phase and structural information of the catalyst. As shown in Figure 2a, the diffraction peaks at 18.5°, 31.3°, 37.3°, 44.19°, 59.35°, and 65.23° were indexed as the (111), (220), (311), (400), (511), and (440) crystal planes belonged to NiCo$_2$O$_4$ nanoparticles. All of the peaks of NiCo$_2$O$_4$
NiCo2O4 nanoparticles on SiO2 powder. The surface area of NiCo2O4, Co3O4, and NiO within the range between 200 and 2000 cm\(^{-1}\). The peaks of NiO can be ascribed to the cubic Pd3m Co3O4, \(\text{Co}_3\text{O}_4\), and NiO within the range between 200 and 2000 cm\(^{-1}\). The peaks of NiCo2O4 at 454, 491, and 644 cm\(^{-1}\) correspond to the \(E_g\), \(F_{2g}\), and \(A_{1g}\) vibrational modes of NiCo2O4, respectively. The peaks of NiCo2O4/SiO2 in the absence of D and G peaks were associated with the carbon structures at 1360 and 1560 cm\(^{-1}\), further confirming that the template was completely burned off during catalyst formation. The \(E_g\), \(F_{2g}\), and \(A_{1g}\) vibrational modes can be attributed to the Co–O bonds in NiCo2O4. The broad intense bands of the characteristic Raman peaks near 500 and 1000 cm\(^{-1}\) were attributed to the Ni–O stretching mode, which corresponds to the reported literature. To further examine the chemical elements and states of the designed catalysts, XPS analysis was applied to investigate the concentration and binding energy of surface atoms present in NiCo2O4 and NiCo2O4/SiO2 component catalyst. As shown in Figure 3a, the high-resolution spectra of Co 2p can be fitted with two spin–orbit doublets and two shakeup satellite peaks. These two spin–orbit doublets with binding energies of 779.28, 781.02, and 782.45 eV belong to Co(II) and Co(III), respectively. The fitting peaks at 857.46, 855.74, and 853.98 eV of Ni 2p are indexed to Ni(III) and Ni(II), respectively (Figure 3b). Furthermore, the fitting of the O 1s spectra (as shown in Figure 3c) at 529.3, 531.2, and 532.1 eV typically correspond to a metal–oxygen bond, oxygen in the cobalt hydroxyl group, and oxygen in the nickel hydroxyl group, respectively, which correspond to the reported literature.

As a porous material, SiO2 supplied an effective adsorption condition for O2 and the reactant, which further increased the oxide efficiency. Thus, SiO2-supported NiCo2O4 can effectively increase the specific surface area of the catalyst, which further improves the catalytic efficiency. As shown in Figure 4a, the surface area has dramatically increased after constructing NiCo2O4 nanoparticles on SiO2 powder. The surface area of NiCo2O4/SiO2 reached 155.86 m\(^2\)/g than that of NiCo2O4 (14.06 m\(^2\)/g). The large specific surface area of NiCo2O4/SiO2 can offer more adsorption and reaction sites than that of NiCo2O4, which further enhanced the 4-methyl guaiacol conversion and vanillin selectivity consequently. 2.2. Excellent Catalytic Activity for Bio-4-Substituted Guaiacol. As a classical representative, bio-4-methyl guaiacol was employed as a model reaction to compare the catalytic activities of NiCo2O4/SiO2, NiO, MnO2, Co3O4, CuO, and Pd(OAc)2 (as summarized in Table 1). At the present, a noble metal ion (such as Pt\(^{2+}\) and Pd\(^{2+}\)) was the most widely used catalyst in oxidation reaction applications. Pd(OAc)2 showed 80.9% conversion for 4-methyl guaiacol. However, the yield for vanillin only reached 46.2% due to inferior selectivity. The primary by-product was vanillic acid, which was generated by over-oxidic reaction. Simultaneously, the scarcity and high cost of noble metal have compelled scientists to reduce the noble metal use. As an effect of the selective oxidizing agent for aldehyde, freshly prepared MnO2 gives only 84.2% conversion with 50.9% selectivity. CuO was the frequently used catalyst for vanillin preparation by the glyoxylic acid method. However, the conversion for 4-methyl guaiacol and selectivity for vanillin were only 79.6 and 48.4%, respectively, when CuO was involved in this catalytic system. Owing to the abundant variable valence, NiO and Co3O4 indicated good catalytic activity for 4-methyl guaiacol. As the coalition of NiO and Co3O4, the catalytic activity of NiCo2O4 was further increased compared with those of the two monomer catalysts attributed to the synergistic effect of Ni(II)
and Co(III). Especially, after being loaded on the porous SiO2 powder, the NiCo2O4/SiO2 composite catalyst exhibited excellent selectivity for vanillin with no vanillic acid detected. This might be attributed to the joint effect of the SiO2 substrate (inhibition of agglomeration for NiCo2O4 and absorption for the reactant). The material conversion achieved nearly 100%, while the vanillin isolated yield reached 86.3%. The gas chromatography (GC) spectra of 4-methyl guaiacol conversion and vanillin generation under the NiCo2O4/SiO2 combined catalyst are shown in Figure S3 (Supporting Information). Further, 4-methyl guaiacol conversion and vanillin generation following time hanging also indicated that vanillin did not decrease after 8 h of stirring.

Employing clean oxidants such as O2 and a recyclable catalyst was an urgent need for efficient methods both in environmental and economic aspects. However, as bio-vanillin was produced in a methanol solvent in the presence of O2, the reaction temperature and maximum tolerant O2 pressure were also important factors for the prospect of bio-vanillin production of the catalyst. The vanillin yield increased from 52 to 86.3% following the temperature increase from 70 to 90 °C. The continuous rise of the temperature (more than 100 °C) caused vanillic acid generation. Vanillic acid and polymer generation following the temperature rise caused the yield to decrease simultaneously. The maximum tolerant O2 pressure following the temperature was detected by a home-made device, as displayed in Figure S4 (Supporting Information). As shown in Figure 4b, the maximum tolerant O2 pressure raised to 0.047 MPa from 0.024 MPa following the temperature variation from 70 to 100 °C in the presence of methanol. To keep the ideal yield and sufficient safety, 90 °C and 0.035 MPa O2 pressure were selected as the optimized conditions for 4-methyl guaiacol oxidation. Furthermore, the mixture temperature raised quickly by 2−3 °C following oxygen blowing at 90 °C due to the oxidation process. With the material consumed, the heat of exothermic reactions and heat dispersion of the system were balanced so that the reaction remained at 90 °C.

In addition, a recycling experiment of this catalyst for 4-methyl guaiacol oxidation was performed to examine the stability of the catalyst. As shown in Figure S5 (Supporting Information), the dominant peaks of Co2+ NiO, NiCo2O4, and NiCo2O4/SiO2 in the IR spectra had no obvious change before and after the oxidation reaction, which indicated the good stability of the catalysts. Simultaneously, the 4-methyl guaiacol conversion and vanillin yield corresponding to the reuse times of NiCo2O4 and NiCo2O4/SiO2 are summarized in Figure 5. The 4-methyl guaiacol conversion stabilized at around 98%, while the yield for vanillin reached 83% in the presence of NiCo2O4/SiO2. Both NiCo2O4 and NiCo2O4/SiO2 maintained excellent catalytic activity during reuse in the six times cycles compared with the yield of vanillin according to NiCo2O4 and NiCo2O4/SiO2. The excellent stability of NiCo2O4/SiO2 may be attributed to the inhibiting effect that prevents the particles of NiCo2O4 from being aggregated. It is worth noting that the vanillin yield decreased to around 76% and the content of the coke pellets increased obviously when NiCo2O4 was employed. This might be attributed to the dispersion of SiO2 inhibiting the peroxidation of NiCo2O4 for the generated vanillin.

Based on the above results, both the NiCo2O4 nanoparticles and the porous SiO2 substrate play positive roles in the enhancement of the 4-substitutional guaiacol catalytic performance. XPS indicated the contents of Co2+ and Ni3+ on the surface of the catalyst. The higher amount of Co2+ and Ni3+ on the surface of NiCo2O4 could accelerate the charge transfer process and lead to the excellent catalytic activity. The possible mechanism is explained as follows: The Ni2+ cation was easily oxidized to Ni3+ due to the stronger oxidizing ability of Co3+, also resulting in the increase in Co2+ content. Then, Co2+ was oxidized by the dissolved oxygen and the generated superoxide anion was absorbed on Ni3+. Under the combined action of Ni3+ cation and superoxide anion, the 4-methyl guaiacol was converted to vanillin. The possible mechanism schematic diagram is presented in Figure 6.

Furthermore, to research the universality to different biomass 4-substrated guaiacols of the catalytic system, ferulic acid, eugenol, and dehydrozingerone were introduced to synthesize bio-vanillin. All of the above biobased 4-substrated guaiacols gave excellent conversion except isoeugenol under such a catalytic condition after 8 h, as summarized in Table 2. The catalytic activity for the oxidation of isoeugenol reacted slowly because of the architectonic difference. As well known, isoeugenol was the mixture of cis- and trans-isomers with the trans-isomer as the dominant isomer. As a result, 35.22% cis-
vanillin from natural vanillin was essential to maintain the summarized. The pMC is the percentage of $^{14}$C content in Technology reference standard SRM 4990C.39,59 The highest the sample relative to the National Institute of Standards and

Figure 6. Possible mechanism schematic diagram for the vanillin generation catalyzed by NiCo$_2$O$_4$/SiO$_2$.

Table 2. Reaction Result Summary from Different Reactants

| material          | conv. (%) | yield (%) | sel. (%) |
|-------------------|-----------|-----------|----------|
| 4-methyl guaiacol | 99.7      | 86.3      | 99.8     |
| 4-ethyl guaiacol  | 92.2      |           |          |
| eugenol           | 99.6      | 69.4      | 99.7     |
| isoeugenol$^a$    | 64.8      | 42.7      | 65.9     |
| dehydrozingerone  | 99.5      | 63.4      | 93.9     |
| ferulic acid      | 100.00    | 57.8      | 87.8     |

$^a$The result was obtained by the reaction for 8 h.

isoegenol was not oxidized into vanillin after 8 h. It should be noted that the residual isoegenol was a cis-isomer, which could be consumed after another 4--8 h. The 4-ethyl guaiacol gave a black polymer at the catalytic system due to the alkenyl polyreaction of high activity. The catalytic system was a middle oxidation condition, which was not powerful enough to split the sp$^3$ C–C bond. After stirring for 8 h, 4-ethyl guaiacol was converted to 4-hydroxy-3-methoxyacetophenone rather than vanillin.

2.3. The Carbon Isotope Investigation for Bio-Vanillin from Different Sources. Effective identification of the bio-vanillin from natural vanillin was essential to maintain the favorable market order.42 The carbon isotope investigation was carried out to examine the difference of the three types of vanillin. As shown in Table 3, the percent modern carbon

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(pMC) values of vanillin from different sources were summarized. The pMC is the percentage of $^{14}$C content in the sample relative to the National Institute of Standards and Technology reference standard SRM 4990C.39,59 The highest $^{14}$C value was detected in living biology because it can acquire $^{14}$C from the atmosphere ceaselessly by photosynthesis. The pMC value of extracted vanillin from vanilla was 99.93, which indicated that vanillin was rooted from natural materials without any fossil fuel mixing. By contrast, the pMC value of the commercial vanillin was 0, which indicated that the vanillin was synthesized from fossil fuels. This is due to the fact that the $^{14}$C in the fossil source was consumed by its radioactivity under million years (half-time of $^{14}$C: 5730 years). It is worth noting that all the pMC values of vanillin from bio-materials (such as 4-methyl guaiacol, ferulic acid, and lignin) were 100%, which is the same as natural vanillin. The activity was also consistent in natural vanillin and bio-material-synthesized vanillin. Furthermore, the pMC value must fall between 0 and 100 in the case of the fossil material-synthesized vanillin doping into natural vanillin or bio-vanillin. However, the pMC value was powerless to distinguish bio-vanillin from natural vanillin on account of the same pMC value. It was necessary to identify bio-vanillin from natural vanillin especially in sophisticated fraudulent practices due to the fact that natural vanillin was much expensive than bio-vanillin.

The $\delta^{13}$C isotope is the stable carbon isotope without radioactivity. Except CO$_2$ in the atmosphere, the $^{13}$C isotope abundance in plants was the highest due to the fact that the $^{13}$C can be transferred to plants by photosynthesis. The $\delta^{13}$C value was mostly affected by the biogenetic pathway (C3, C4, or CAM) and by environmental factors (such as CO$_2$ density, rainfall, temperature, and so on). Thus, the $\delta^{13}$C value was different in botanical precursors, which further caused the various $\delta^{13}$C values of bio-vanillin according to the reported literature.60,61 In the photosynthesis process, the value of $\delta^{13}$C falls between $-24\%e$ and $-34\%e$ in C3 plants (Calvin cycle), while the value increased to $-10\%e$ to $-16\%e$ in C4 plants (hatch-hatch cycle). Furthermore, the $\delta^{13}$C value of fossil source-synthesized vanillin somewhere between $-24\%e$ and $-31\%e$ was attributed to the precursors derived from many ancient creatures. It was useful to trace or identify the vanillin source by the $^{13}$C isotope.62,63

To investigate the connection between bio-vanillin and the material for vanillin, the $\delta^{13}$C value of bio-vanillin from biomass was tested to supply a reference information for the normalization of vanillin. As shown in Table 3, the $^{13}$C isotope information of different sources was examined based on VPDB. The $\delta^{13}$C value for natural vanillin was $-19.6\%e$, which belongs to the classical CAM cycle. The $\delta^{13}$C value of bio-vanillin synthesized from 4-methyl guaiacol, eugenol, ferulic acid, and lignin was between $-24\%e$ and $-34\%e$, which further showed the material rooted from C3 plants. Vanillin from ferulic acid had the lowest $\delta^{13}$C value ($-37.0\%e$), while vanillin from 4-methyl guaiacol had the highest value ($-25.2\%e$). Besides, the $^{14}$C examination indicated that commercial vanillin was a biomass-free product, and the $\delta^{13}$C result ($-25.5\%e$) further confirmed the fossil source.

3. CONCLUSIONS

To sum up, a high-efficiency catalytic oxidation method was carried out in CH$_3$OH by employing a non-noble metal oxide combined catalyst (NiCo$_2$O$_4$/SiO$_2$) for bio-vanillin preparation from biobased 4-substituted guaiacol. The catalytic system has universal applicability to a variety of natural 4-substituted guaiacols, and the isolated yield of vanillin reached 86%, which provides theoretical guidance for the research of the production process of bio-vanillin. More importantly, the C isotope of prepared bio-vanillin from different natural raw materials was investigated. The $^{14}$C isotope accurately showed
that all the prepared bio-vanillin was derived from natural products, and the $^{13}$C isotope determines the material source of biomass vanillin. It provides an effective method for the identification and classification of bio-products, which provides a theoretical basis for regulating the market of bio-vanillin.

4. EXPERIMENTAL SECTION

4.1. Reagent and Materials. 2-Methoxy-4-methylphenol, eugenol, isoeugenol, ferulic acid, dehydrozingerone, methanol, sodium hydroxide, acetonitrile, urea, ethanol, hexadecyl trimethyl ammonium bromide (CTMBA), tetrathyl orthosilicate (TEOS), Ni(OAc)$_2$, and Co(OAc)$_2$ were purchased from Sino Pharma Chemical Reagent Co., Ltd. Lignin was purchased from Borregaard LignoTech Co., Ltd. X-ray data on suitable single crystals were collected at 293(2) K with a Focus D8 (Bruker, Germany) with Cu K$_\alpha$ radiation ($\lambda = 0.1542$ nm). The composition and structure of these catalyst samples were investigated using a Raman spectrometer (DXR, Thermo Fisher Scientific, America). The morphology of the as-prepared catalyst was characterized by field-emission scanning electron microscopy (Regulus 8100, Hitachi, Japan). Transmission electron microscopy (TEM) was carried out on HF5000 Hitachi. The X-ray photoelectron spectroscopy (XPS) experiments were performed on a Thermo Escalab 250Xi system using Al K$_\alpha$ radiation ($h\nu = 1486.6$ eV). The Brunauer–Emmett–Teller (BET) specific surface areas of typical products were obtained at 77 K in a Micromeritics ASAP 2020 system. The oxidations were performed on an autoclave reactor (1000 mL, Weihai Automatic Reaction Kettle Co., Ltd.). Gas chromatography (GC7890) and high-performance liquid chromatography (HPLC-Ulti Mate 3000, Thermo Fisher Scientific) were employed to detect material conversion.

4.2. Preparation of Co$_3$O$_4$, NiO, NiCo$_2$O$_4$, and NiCo$_2$O$_4$/SiO$_2$. 4.2.1. Preparation of NiCo$_2$O$_4$ and NiCo$_2$O$_4$/SiO$_2$. In a typical synthetic procedure, Co(OAc)$_2$ (3.54 g, 20 mmol), Ni(OAc)$_2$ (1.77 g, 10 mmol), and urea (3.0 g, 50 mmol) were completely dissolved in deionized water (350 mL) under vigorous stirring at room temperature. The mixture was then transferred into a 500 mL autoclave and then hydrothermally heated at 120 °C for 4 h in an oven with constant stirring. The mixture was cooled to room temperature, filtered, washed with deionized water, and dried in vacuum at 40 °C for 4 h. Half of the residue solid was calcined at 500 °C in air for 6 h to give NiCo$_2$O$_4$ nanoparticles. The remaining half of the residue solid was added to 500 mL flasks with water (50 mL), ethanol (300 mL), CTMAB (10.0 g, 0.0274 mol), and TEOS (35.0 g, 0.168 mol). After the dropwise addition of ammonia water (100 mL) at 45 °C, the reaction mixture was stirred for 6 h. Then, the mixture was filtered, 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 a NiCo$_2$O$_4$/SiO$_2$ nanoparticle catalyst.

4.2.2. Preparation of Co$_3$O$_4$. Co(OAc)$_2$ (3.54 g, 20 mmol), CTMAB (10.0 g, 0.0274 mol), and urea (3.0 g, 50 mmol) were completely dissolved in deionized water (250 mL) under vigorous stirring at 40 °C, and the temperature was raised to 80 °C and kept for 1 h. Then, the solids were filtered, washed with water, and dried in vacuum at 70 °C. After the solids were continuously thermally treated in air at 200 °C for 1 h, they were heated up to 350 °C for 2 h in a muffle furnace to obtain the pure Co$_3$O$_4$.

4.2.3. Preparation of NiO. Ni(OAc)$_2$ (1.77 g, 10 mmol) and ethyl alcohol were completely dissolved in deionized water (250 mL) under vigorous stirring at 50 °C for 2 h. A homogeneous solution of citric acid was also prepared in ethanol and slowly added to the nickel nitrate solution. The liquor was heated to make the solution colloidal. The solution colloidal sample was annealed at 600 °C and NiO was obtained.

4.3. Regeneration of Catalyst. For regeneration, the spent catalysts are collected, washed with ethanol, and dried at 40 °C in vacuum. The solid was calcined in 500 °C for 3 h.

4.4. The High-Efficiency Conversion of Natural Materials. A solution of natural 4-methyl guaiacol (41.5 g, 0.3 mol) in methanol (400 mL) was added to a 1000 mL autoclave reactor. After NaOH (60.0 g, 1.5 mol) was added portion-wise to the above solution with sustained stirring, NiCo$_2$O$_4$ (0.25 g) was added. The sealed autoclave reactor was then heated to 90 °C, and then underwent O$_2$ blowing to keep the O$_2$ pressure at 0.035 MPa. After stirring for 8 h, the mixture was filtered and concentrated in vacuum. The residue was recrystallized with ethanol/water (1:3 wt %, 110 mL) to give a white needle solid (57.1 g; yield: 96.1%).

4.4.1. Bio-Vanillin Preparation from Lignin. In a 1000 mL autoclave reactor, lignin (40 g), NiCo$_2$O$_4$/SiO$_2$ (0.5 g), and a solution of NaOH (40.0 g, 1.0 mol) in water (400 mL) were added. The mixture was heated to 170 °C and the pressure reached 0.63 MPa. Then, the system was replenished with O$_2$ to keep the pressure at 0.93 MPa. After stirring for 2 h, the mixture was cooled down to room temperature and acidified to pH 2 with 2 M aq. HCl. The mixture was extracted with chloroform (100 mL × 3). The combined organic layers were washed with brine (100 mL), dried over MgSO$_4$, and concentrated in vacuum. The residue was purified by silica gel chromatography (petroleum ether/ethyl acetate = 10:1 to 2:1) to give the natural vanillin as a white needle crystal (350 mg).

4.5. The Extraction of Natural Vanillin. Vanilla beans (10 g) were ground into powder and then added to a round-bottom flask containing 100 mL of ethanol. After ultrasonication for 30 min, the suspension was heated to 90 °C and refluxed for 2 h. The mixture was filtered and concentrated in vacuum to give a brown residue. The residue was added to 1 M NaOH (40 mL) and washed with dichloromethane (40 mL). The pH value of the aqueous phase was adjusted to 4 by 1 M hydrochloric acid, and then the residue was extracted with ethyl acetate (40 mL × 3). The combined organic layers were washed with brine, dried over MgSO$_4$, and concentrated in vacuum. The residue was purified by prep-TLC (petroleum ether/ethyl acetate = 4:1) to give the natural vanillin as a white needle crystal (110 mg; yield: 1.1%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00370. Structure of lignin macromolecule; gas chromatography spectrum of the reaction; energy-dispersive spectroscopy.
of NiCo₂O₄ and NiCo₂O₄/SiO₂; device sketches of tolerance detection for O₃ pressure; and infrared spectra of NiCo₂O₄/SiO₂, NiCo₂O₄, Co₂O₄, and NiO (PDF)

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Notes
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