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Oxidation of biomass-derived furans to maleic acid over nitrogendoped carbon catalysts under the acid-free condition

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Maleic acid (MA) is a platform chemical used for synthesizing high-value polymers. Although MA can be produced from biomass-derived furfural, so far, only acidic catalysts have been proposed. Herein, for the first time, we report an acid-free furfural-to-MA conversion using nitrogen-doped carbon (NC) as an effective catalyst with the assistance of hydrogen peroxide (H_2O_2) oxidant. High MA yield (61 %) can be achieved over the NC-900 catalyst at 80 °C. The effects of reaction conditions, including H_2O_2 concentration, solvent type, reaction temperature, and time were systematically studied in detail and optimized. The ZIF-8-derived NC catalyst exhibited high activity owing to the existence of high graphitic nitrogen (N-Q) content in the carbon framework. The kinetics study indicates that the oxidation of furfural to MA over the NC-900 catalyst is via the formation of the 5-hydroxy-furan-2(5H)-one as the main intermediate. Further, the NC-900 can convert a variety of biomass-derived furan compounds to MA under acid-free conditions, indicating the versatility and applicability of the present acid-free, NC-based catalytic system.

Introduction

To reduce the dependence on fossil resources, the use of sustainable and renewable resources for producing high-value chemicals and liquid hydrocarbons have been constantly increasing in the past decade.1-4 Biomass-derived furan compounds, generally produced via hydrolysis followed by dehydration reactions of cellulose and hemicellulose, are considered as one of the most important renewable chemicals.⁵⁻¹² Many high-value products or starting chemicals in industrial manufacture can be synthesized from the furan compounds such as tetrahydrofurfuryl alcohol, 2-methyl furan, 2,5-dimethyl furan, etc. by different catalytic reactions.9, 13-15 Among them, the C4 di-acids or anhydride (succinic acid (SA), maleic acid (MA), and maleic anhydride (MAN)) are important starting chemicals in polymer, pharmaceutical, and chemical industries. $^{9,\ 16\text{-}19}$ These chemicals were used to produce polymers, unsaturated polyester resins, vinyl copolymers, lubricant additives, plastics, and solvents, including y-1,4-butanediol butvrolactone (GBL), (1,4-BDO) and tetrahydrofuran (THF).18 Thus, the conversion of biomassderived furans into C4 di-acids or anhydride has become an important research topic.^{9, 20}

MA has the highest annual production (1.8 million tons per year), compared to fumaric acid (0.09 million tons per year) and succinic acid (0.03 million tons per year),²¹ and the synthesis of MA generally based on the products of crude oil refinery (i.e. benzene, butane), which is an exhaustible and non-renewable feedstock. Therefore, an alternative pathway for producing MA from a renewable resource is highly demanded.

Recently many reports showed the MA production using furfural oxidation in either gas or liquid phase media.²¹⁻²⁵ Gou et al. reported the use of phosphomolybdic acid (homogeneous catalyst) in a biphasic solvent system at 110 °C (2 MPa O2 pressure) for the aerobic oxidation of furfural to MA.22 Nevertheless, a harsh condition such as high O₂ pressure (2 MPa) and a relatively low yield of MA (34.5%) are the drawbacks of the proposed system.²² Recently, the catalytic oxidation of furfural to MA can be carried out under mild conditions using liquid oxidant (H₂O₂), which also significantly improved the MA yield. However, these methods require either betaine hydrochloride (BHC) or formic acid (4 mL for 1 mmol of furfural) as a catalyst in large concentration.^{21, 24} Araji et al. and coworkers investigated the possibility of using betaine hydrochloride (BHC) as the catalyst for furfural oxidation with the assistance of H_2O_2 as an oxidant to produce MA (61%) and fumaric acid (FA 31%) within 30 min at 100 °C.²¹ Further, the use of a solid acid catalyst such as titanium silicate is also reported for the oxidation of furfural to MA.²³ In this case, the highest yield of 78% MA was obtained at 50 °C within 24 h.23 Although these homogeneous and heterogeneous acidic catalysts showing good catalytic activity for the furfural oxidation, these acid catalysts have their own drawbacks such as metal leaching during the reaction and product purification

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issues. Therefore, an acid-free environmentally friendly catalytic system for furfural-to-MA conversion has been scientifically challenging and industrially important.

Recently, MOF-derived carbon materials have become an excellent material for many applications due to their extraordinary properties.²⁶⁻²⁹ Among them, ZIF-8-derived N-doped porous carbon shows significant catalytic applications since it exhibits extremely high surface area, uniform morphology, higher N content as active sites, etc.³⁰⁻³³ Besides, NC is an environmentally benign catalyst and shows superior catalytic activity in the oxidation reaction.¹⁴ Thus, the NC is considered as a promising catalyst in many catalytic applications.

Therefore, to overcome the drawbacks of present acidbased furfural oxidation to MA and considering significant advantages of NC materials we aim for the oxidation of furfural to MA using NC catalyst and H₂O₂ as a liquid oxidant under mild reaction acid-free condition. The synthesis and characterization of the ZIF-8-derived NC catalyst were described and discussed in our previous report (please see Supporting Information, Fig. S1-S4, and Table S1). $^{\rm 14}$ In this work, we mainly study the catalytic performance of NC for the oxidation of furfural to MA. The effect of various reaction parameters such as calcination temperature, H₂O₂ concentrations, solvent, temperatures, and the reaction time was systematically studied in detail for the furfural oxidation to MA. Furthermore, apart from furfural other furan compounds such as furan, 5-hydroxymethylfurfural (HMF), furoic acid, and 2,5-furandicarboxylic acid (FDCA) were also tested for the reaction to extend the application of present study for various biomass-derived furan compounds. We also investigated the reaction pathway for the furfural oxidation to MA over NC catalyst and further compared the activity of ZIF-8derived NC with graphitic carbon nitride and NC-derived from biomass to investigate the efficiency of ZIF-8-derived NC. The role of nitrogen content and type of nitrogen (pyridinic (N-6), pyrrolic (N-5) and graphitic nitrogen (N-Q)) were also investigated using XPS analysis for the oxidation of furfural to MA to find the actual active sites in the NC catalyst.

Experimental

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Materials and methods

Zinc nitrate hexahydrate (98%), 2-methylimidazole (99%), 5hydroxymethylfurfural (HMF; 99%), 2,5-furandicarboxylic acid (FDCA; 99%) Maleic acid (MA; 99%) succinic acid (SA; 99%), 2furoic acid (99%), furan (99%), melamine (99), and chitosan were purchased from Sigma-Aldrich, while furfural (99%), hydrogen peroxide (H_2O_2 ; 35%), and fumaric acid were procured from Acros Organics. The polyvinylpyrrolidone K-30 (PVP) received from TCI, and all chemicals were used without any further purification.

The liquid-phase oxidation of furfural to MA was carried out in a round bottom flask connected with a reflux condenser. Typically, an 83 μ L furfural (1 mmol) and 50 mg catalyst were added into a 25 mL three-neck flask containing 5 mL of water. The mixture was stirred for 2 min and then 5 mL H₂O₂ (35 wt%) was added to it. Further, the reaction mixture was heated to the desired temperature under magnetic stirring in a closed system. After completion of the reaction, the reaction solution of the reaction was cooled to room temperature and diluted into 25 mL with deionized water. The solution was then filtered using a syringe filter (0.22 μ m pore size) for HPLC analysis.

Catalyst preparation

Synthesis of ZIF-8-derived N-doped carbon

Nitrogen-doped porous carbons were synthesized analogous to the previous literature.¹⁴ As-synthesized ZIF-8 powders were calcined under N₂ atmosphere at given temperatures (600, 700, 800, and 900 °C) for 8 h with a heating rate of 5 °C·min⁻¹. After carbonization, the samples were washed thoroughly with concentrated HCl (36.5%) to remove the residual zinc components. Finally, the resulting samples were purified by washing with deionized water and methanol for several times and activated at 150 °C for 5 h before each catalytic reaction. The samples were named to be NC-x, where x represents the calcination temperature of 600, 700, 800, and 900 °C, respectively.

Synthesis of graphitic carbon nitride

Graphitic carbon nitride $(g-C_3N_4)$ was synthesized according to the reported literature.³⁴ The melamine powder (10 g) was placed in a crucible and heated under air at 520 °C to 4 h with a heating rate of 10 °C min⁻¹. After 4 h, the furnace was cooled to room temperature. The yellow-colored powder was collected and used for the catalytic oxidation of furfural.

Synthesis of N-doped carbon from biomass

The nitrogen-doped carbon material from biomass was synthesized according to the reported study with slight modification.³⁵ First, the urea (12 g) was dissolved in water (10 mL), then chitosan (1 g) was added slowly to the urea solution under vigorous stirring. Once the complete dispersion of chitosan is achieved, the acetic acid (500 μ L) was added under vigorous stirring for 30 min to attain a semi-transparent homogeneous paste. Further, the sample was dried at 70 °C for 16 h resulted in the formation of white solid. This solid material was then calcined at 900 °C under N₂ atmosphere to 5 h, with a heating rate of 3 °C min⁻¹.

Catalyst characterization and Products analysis

Powder X-ray diffraction (XRD) analysis was carried out with a Rigaku-Ultima IV instrument using Cu K α (λ =1.5406 Å) radiation (40 kV voltage). Diffraction patterns were recorded within a 20 range of 10-80° with a 20° min⁻¹ scanning rate. The chemical state of nitrogen and carbon (N 1s and C 1s) was analyzed using X-ray photoelectron spectroscopy (XPS), Thermo Scientific, Theta Probe. To compensate for the surface charge effect, binding energies were calibrated using the C 1s hydrocarbon peak at 284.60 eV. The elemental composition of samples (carbon and nitrogen) was analyzed using the Elemental Vario EL cube instrument. The N₂-adsorption-desorption analysis was performed using the BELSORP series (II) instrument. Detail characterization of ZIF-8 and ZIF-8-derived NC was discussed in our previous study ¹⁴.

The high-pressure liquid chromatography (HPLC) equipped with a refractive index detector and ICE-Coregel 87H3 column was used for the analysis of reaction mixture. External standard

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calibration curves were utilized to calculate the concentration of furfural and all other products. The HPLC operated using the aqueous solution of 8 mM sulfuric acid as a mobile phase with a flow rate of 0.6 mL min⁻¹ and the column oven temperature was kept at 35 °C during analysis.

The conversion and product yield are calculated by the following formulae.

Furfural conversion (%) = $\frac{\text{Moles of furfural reacted}}{\text{Initial moles of furfural}} X 100$

Product yield (%) = $\frac{\text{Moles of product formed}}{\text{Initial moles of furfural}} X 100$

Results and discussion

Initially, the catalyst evaluation study was carried out with various catalysts for the oxidation of furfural to MA under the assistance of liquid oxygen (H_2O_2) as oxidant. As shown in Table 1, a high furfural conversion (from 98 to 100%) achieved at all tested catalysts. However, the desired product yield (MA) is significantly lower (9-34%) without catalyst and with acid catalysts (Table 1, entry 1-7). Besides, succinic acid (SA) is produced along with MA, showing that the catalytic oxidation of furfural using acid catalyst has less selectivity for the MA.^{36, 37} In contrast, a high MA yield is achieved over the NC-x catalysts, which was in the range of 40 to 61% within 5 h reaction time (Table 1, entry 8-11). Moreover, with NC catalysts, the yield of SA is extremely low (<9%), confirming that NC-x catalysts are highly active in converting furfural to MA. For comparison, we used activated carbon (AC) and graphite as a catalyst for furfural oxidation to MA under similar reaction conditions. The results showed only 16% and 17% MA yield in the presence of AC and graphite catalysts without nitrogen content, respectively (Table 1, entry 12-13). Furthermore, the ZIF-8 catalyst showed a 25% MA yield along with an 18% SA yield (Table 1, entry 14). These results suggest that nitrogen content in porous carbon played an important role in converting furfural to MA with higher selectivity. The activity of furfural oxidation using ZIF-8 and HCI showed 25 and 34% MA yield, while the NC-900 catalyst showed 61% MA yield, suggesting that NC-900 catalyst can show an almost two-fold increase in MA yield under acid-free and metalfree condition.

As shown in Table 1 (entry 8-11), the effect of nitrogen content in the NC-x catalysts and calcination temperature was investigated for the oxidation of furfural to MA. The gradual increase of MA yield was observed by increasing the calcination temperature from 600 to 900 °C for the ZIF-8 derived NC catalyst (NC-600, 40%; NC-700, 53%; NC-800, 58%; and NC-900, 61%) (Table 1, entry 8-11). However, the increase of MA yield was not consistent with the total amount of nitrogen content in the catalysts (Fig 1b). Further, we investigate the relationship between the concentration of N-Q, N-5, and N-6 species in the NC catalysts with a yield of MA (Fig. 1a, 1c, and 1d) to understand the effect of type of N species on the furfural oxidation. It is found that the concentration of N-Q species is in linear proportion to the MA yield (Fig. 1a), whereas, N-5 species

do not show any relation to the MA yield, and the MA yield decreases with increase in the concentration of NOS species (Fig. 1c and 1d), suggesting that the N-Q species is important active site for the selective oxidation of furfural to MA. Besides, the surface area of NC-x catalysts could contribute to the catalytic oxidation of furfural to MA. Fig. S5 (ESI) shows the relationship between the surface area of the NC-x catalyst and the MA yield. The results indicate that the surface area and MA yield were not linear with the MA yield. Although NC-700 catalyst and NC-900 catalyst has almost similar BET surface area (NC-700 = 795 m² g^{-1} ; NC-900 = 813 m² g^{-1}), the NC-700 showed lower MA yield (53%) compared to NC-900 (61%). Further, the ZIF-8 has a very high BET specific surface area (1428 m² g⁻¹) compared to the NC-900 catalyst. However, it showed lower MA yield (25%) than NC-900 catalyst (61%), suggesting that the surface area of the NC-x catalyst does not play an important role in catalytic oxidation of furfural to MA

Table 1: Aerobic oxidation furfural to maleic acid under various catalysts

EntryCatalystsConversion (%)Maleic acid Yield (%)Succinic acid Yield (%)1-10015152Zn(NO_3)210013183ZnO1009264 H_2SO_4 9817105HCI98.534226 CH_3COOH 10017177 $Amberlyst-$ 159816138NC-9001006139NC-80010058210NC-70010053311NC-60010040912AC98.6161113Graphite991714					
1-10015152 $Zn(NO_3)_2$ 10013183 ZnO 1009264 H_2SO_4 9817105HCI98.534226 CH_3COOH 10017177 $Amberlyst-$ 159816138NC-9001006139NC-80010058210NC-70010053311NC-60010040912AC98.6161113Graphite991714	Entry	Catalysts	Conversion (%)	Maleic acid Yield (%)	Succinic acid Yield (%)
2 $Zn(NO_3)_2$ 10013183 ZnO 1009264 H_2SO_4 9817105HCI98.534226 CH_3COOH 10017177 $Amberlyst$ 9816138NC-9001006139NC-80010058210NC-70010053311NC-60010040912AC98.6161113Graphite991714	1	-	100	15	15
3 ZnO 1009264 H_2SO_4 9817105HCl98.534226 CH_3COOH 10017177 $Amberlyst-$ 159816138NC-9001006139NC-80010058210NC-70010053311NC-60010040912AC98.6161113Graphite991714	2	Zn(NO ₃) ₂	100	13	18
4 H_2SO_4 9817105HCI98.534226 CH_3COOH 10017177 $Amberlyst-$ 159816138NC-9001006139NC-80010058210NC-70010053311NC-60010040912AC98.6161113Graphite991714	3	ZnO	100	9	26
5HCI98.5 34 22 6CH ₃ COOH10017177 $A^{mberlyst-}_{15}$ 9816138NC-9001006139NC-80010058210NC-70010053311NC-60010040912AC98.6161113Graphite991714	4	H_2SO_4	98	17	10
6 CH ₃ COOH 100 17 17 7 Amberlyst- 15 98 16 13 8 NC-900 100 61 3 9 NC-800 100 58 2 10 NC-700 100 53 3 11 NC-600 100 40 9 12 AC 98.6 16 11 13 Graphite 99 17 14	5	HCI	98.5	34	22
7 Amberlyst- 15 98 16 13 8 NC-900 100 61 3 9 NC-800 100 58 2 10 NC-700 100 53 3 11 NC-600 100 40 9 12 AC 98.6 16 11 13 Graphite 99 17 14	6	CH₃COOH	100	17	17
8 NC-900 100 61 3 9 NC-800 100 58 2 10 NC-700 100 53 3 11 NC-600 100 40 9 12 AC 98.6 16 11 13 Graphite 99 17 14	7	Amberlyst- 15	98	16	13
9 NC-800 100 58 2 10 NC-700 100 53 3 11 NC-600 100 40 9 12 AC 98.6 16 11 13 Graphite 99 17 14	8	NC-900	100	61	3
10 NC-700 100 53 3 11 NC-600 100 40 9 12 AC 98.6 16 11 13 Graphite 99 17 14	9	NC-800	100	58	2
11 NC-600 100 40 9 12 AC 98.6 16 11 13 Graphite 99 17 14	10	NC-700	100	53	3
12 AC 98.6 16 11 13 Graphite 99 17 14	11	NC-600	100	40	9
13 Graphite 99 17 14	12	AC	98.6	16	11
	13	Graphite	99	17	14
14 ZIF-8 100 25 18	14	ZIF-8	100	25	18

Reaction condition: Furfural (1 mmol), H_2O (5 mL), catalysts (50 mg), H_2O_2 (5 mL; 35 wt%), time 5 h, temperature 80 °C.

Gao et al. demonstrated that the graphitic N atom acts as a promotor to stimulate the chemical reactivity of its adjacent carbon atoms and favors the formation of oxygen radicles after reacting with H_2O_2 , which is active sites for the furfural oxidation.³⁸ To confirm this reactive oxygen species in our reaction system, we examined the chemical state of C 1s in the NC-900 catalyst using XPS analysis. Fig. 1e and 1f represent the bonding types of NC-900 catalysts with and without H_2O_2 treatment (NC-900- H_2O_2 and fresh NC-900). Based on highresolution XPS characterization, the formation of new chemical

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bonding (C-O-OH) in case of C 1s chemical status of h_{1} C-900 $H_{2}O_{2}$ was observed.³⁹⁻⁴¹ It is reported that the performed species (-O-OH) exhibited higher catalytic activity for the oxidation reaction.^{24, 38} The formation of the reactive oxygen



Fig. 1 Relationship of MA yield with a) N-Q (wt%), b) total amount of N, c) N-5 (wt%) appedies of the presence of the presence

Effect of reaction conditions on catalytic oxidation of furfural

The liquid oxidant H₂O₂ could be decomposed in the presence of NC catalyst that promoted the formation of reactive oxygen species because of the presence of graphitic N, as shown in Fig. $1f.^{23, 42}$ Thus, the effect of H_2O_2 concentration on furfural oxidation has been considered. A different H₂O₂ concentration (15%, 20%, 25%, and 30%) was tested for the reaction along with the NC-900 catalyst. The reaction carried out without the addition of H_2O_2 is not able to show the formation of MA. Besides, MA formation was not observed when furfural oxidation was carried out in the presence of air and pure oxygen (flow rate 40 mL min⁻¹) at 80 °C. As shown in Fig. 2, the MA yield strongly dependent on the H₂O₂ concentration. The gradual increase of H₂O₂ concentration from 15% to 35% results in the increase in MA yield from 41% to 61%, respectively. Interestingly, the yield of SA co-product remains unchanged with increasing H₂O₂ concentration to be ca. 2%. Besides, a 38% residual formed for a reaction carried out with 35% H₂O₂ could be intermediate products or side products due to the decomposition and polymerization of furfural. Some intermediates identified using HPLC analysis of the reaction mixture by injecting standards of possible products such as fumaric acid (FA), furoic acid, 5-Hydroxy-2(5H)-furanone (hydroxyfuranone), and 2-(H)-furanone, respectively (Fig. S6; ESI). Further, we have carried out the furfural oxidation into MA that the presence of N-Q species in NC-x catalysts is important with increasing the forfural concentration from 1 mmol to 5 mmol. The result showed almost similar MA yield (56%) without increasing the H_2O_2 concentration, suggesting that the use of higher substrate concentration can help to decrease the oxidant (H_2O_2) to substrate ratio to some extent.



Fig. 2 Influence of H_2O_2 concentration on the furfural oxidation over NC-900 as catalyst; Reaction condition: furfural (1 mmol), catalyst (50 mg), water 5 mL, time 5 h, temperature 80 °C.

Further, we investigated the effect of various solvent on the furfural oxidation including water (H_2O) , dimethylformamide

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(DMF), dimethyl sulfoxide (DMSO), dimethylamine (DMA), diethylene glycol dimethyl ether (Diglyme), and ethanol. As shown in Fig. 3, low MA yield obtained in the range from 2-17% in organic solvents. On the other hand, the water solvent showed a surprisingly high yield of MA (61%) and low yield of SA (3%). These results indicate that the organic solvent systems are not efficient for the furfural oxidation, and water is the superior solvent system than organic solvents as it promotes the higher MA yield.^{22, 23} Since the water media can provide a suitable environment for the decomposition of H₂O₂ and promote the formation of peroxide like species (-OOH), further, H₂O₂ in water form water and oxygen gas which is more stable than original H₂O₂.



Fig. 3 The furfural oxidation under various solvents; Reaction condition: furfural (1 mmol), NC-900 catalyst (50 mg), solvent 5 mL, H_2O_2 5 mL (35 wt%), time 5 h, Temperature 80 °C,

In the kinetic point of view, reaction temperature extremely affects the selectivity of the desired product in various reactions.^{43, 44} Hence, the furfural oxidation was carried out at different temperatures such as 40 °C, 60 °C, 80 °C, and 90 °C using NC-900 catalyst in aqueous media (Fig. 4). The results showed that the selective catalytic furfural oxidation to MA over the ZIF-8-derived NC-900 catalyst extensively depends on the reaction temperature. Although the furfural conversion is 100% at all tested reaction temperatures, the selectivity of MA changes significantly in various reaction conditions. As shown in Fig. 4, only 23% MA yield could be obtained within 5 h at 40 °C. The highest MA yield (61%) was achieved when the reaction was carried out at 80 ºC. Besides, further increasing reaction temperature to 90 °C results in the decrease of MA yield to 54%, suggesting the decomposition of furfural due to the formation of side products at high temperature. Thus, the optimal reaction temperature for furfural oxidation to MA catalysed by the NC-900 catalyst is 80 °C which also offers higher MA selectivity.



Fig. 4 Effect of reaction temperature on the furfural oxidation; Reaction condition: furfural (1 mmol), NC-900 catalyst (50 mg), water 5 mL, $H_2O_2 5$ mL (35 wt%), time 5 h.

Mechanism of catalytic oxidation of furfural over NC-900

To study the kinetics of the catalytic oxidation of furfural over NC-900 catalyst under acid-free condition using H₂O₂ as oxidant, the time-dependence of the reaction was studied at 80 °C. The reaction pathway was studied by analyzing intermediate products at the variation of reaction time combined with the previous literature and our obtained results. The changes in the product distribution show that 96% of furfural was consumed in 1 h, as shown in Fig. 5. At the same time, the MA and 5-hydroxyfuran-2(5H)-one were produced with the dominant yield of 26% and 41% compared to SA (ca. 1%) and 2-(5H)-furanone (0.5%), respectively. Further, an increase in reaction time leads to a decrease of 5-hydroxyl-furan-2(5H)-one yield and dramatic improvement in the MA yield (Fig. 5), suggesting that the 5hydroxy-furan-2(5H)-one was converted to MA. After 5 h reaction, the 5-hydroxyl-furan-2(5H)-one intermediate is completely consumed while the MA yield approaches the highest value (61%). On the other hand, the formation of SA (2%) and 2-(5H)-furanone (5%) was extremely slow under similar reaction conditions, suggesting that the reaction proceeds mainly through 5-hydroxy-furan-2(5H)-one intermediate. The residue of 33% yield contributed to side products such as small amounts of fumaric acid (FA), furoic acid, formic acid, furan-2(5H)-one and maybe some unknown side products due to the polymerization and decomposition reactions of furfural, as shown in Fig. S6.

It was reported that the furfural oxidation to MA could be via the formation of 2-(5H)-furanone as an intermediate product, which is further converted to MA.^{23, 45} However, this pathway can be eliminated in the present reaction system because of the very low yield/selectivity of 2-(5H)-furanone intermediate over NC-900 catalyst (Fig. 5). Additionally, we have carried out oxidation using the 2-(5H)-furanone (intermediate) as a reactant under similar reaction conditions, instead of furfural, the result showed a small amount of SA production and no MA yield in 5 h. On the other hand, the 5-

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hydroxy-furan-2(5H)-one is the dominant product in 1 h reaction, which is then converted to MA. Thus, we speculate that the major reaction pathway of furfural oxidation using NC-900 as catalyst and H_2O_2 as oxidant should be via the formation 5-hydroxy-furan-2(5H)-one as a main intermediate product (Scheme 1), as proposed by Granados's and Jacobs's group.^{23, 46} The inferior yield of 2-(5H)-furanone intermediate and lower possibility of its conversion to MA, suggests the reaction A pathway is less significant (Scheme 1).

Fig, 5 Reaction kinetics of the furfural oxidation; Reaction condition: furfural (1



mmol), NC-900 catalyst (50 mg), water 5 mL, $\rm H_2O_2$ 5 mL (35 wt%), temperature 80 $^{\rm 9}\rm C.$

As shown in Scheme 1, the furfural oxidation in the presence of NC-900 as a catalyst and H_2O_2 as an oxidizing agent could show two possible reaction pathways at the same time. Pathway A is the minor pathway to form the side product such as SA. In contrast, the major reaction pathway is ascribed to the pathway B, in which the furfural undergoes a series of reactions including the oxidative ring-opening reaction, Baeyer-Villiger oxidation, rearrangement steps, and hydrolysis to form 5hydroxy-furan-2(5H)-one as the main intermediate. Subsequently, the 5-hydroxy-furan-2(5H)-one was oxidized to MA, as shown in Fig. 5.

As above demonstrated, the adjacent carbon atoms to N-Q sites in the nitrogen-doped carbon catalyst could form the reactive oxygen species, which served as active sites for converting furfural to MA. It is reported that N-doped graphitic catalysts can generate reactive oxygen species in presence of H₂O₂ oxidant.^{38, 42, 47-49} To address this point and free radical mechanism, we carried out the reaction with and without the addition of Gallic acid as scavenging agent.⁵⁰ As shown in Fig. S7; ESI, a lower MA yield of 34% could be obtained in the presence of Gallic acid as a scavenging agent, compared to 61% MA in the absence of the scavenging agent. This result confirms that the furfural oxidation into MA using H₂O₂ as an oxidant follows the radical mechanism. This observation is in good agreement with the above-obtained results. Overall, hydrogen peroxide decomposed to radicals which coordinate with adjacent carbon atoms to graphitic-type nitrogen dopant in NC to form reactive oxygen species as catalytic active sites, as confirmed with XPS analysis (Fig 1f). Subsequently, the furfural interacted with the reactive oxygen species and oxidized into MA via oxidative ring-opening, Baeyer-Villiger oxidation, and hydrolysis. Besides, the kinetic study showed that the furfural oxidation into MA over the N-doped carbon catalyst was proceeding through the formation of 5-hydroxy-furan-2(5H)one as the main intermediate product, this showed that reaction happens through B reaction pathway (Scheme 1).



Scheme 1 The reaction pathway of catalytic furfural oxidation over NC-900 acid-free catalyst.

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To understand the reusability of the NC-900 catalyst, we carried out the recycle experiments with NC-900 catalyst underoptimized reaction conditions. As shown in Fig. 6, although the furfural conversion remains unchanged during the recycling test, the MA yield gradually decreased from 61% to 40% after the fourth run, suggesting that the instability of the catalyst under the reaction environment. To understand the nature of active sites of the catalyst after the recycling experiment, we performed the XPS analysis of fresh and spent catalysts. As shown in Fig. S2 and Fig. S8, the N 1s of the fresh NC-900 was deconvoluted into three peaks, corresponding to pyridinic-N (N-6 at 398.4 eV), pyrrolic-N (N-5 at 399.8 eV), and quaternary (N-Q at 401.1 eV) (Fig. S2; ESI).^{14, 51} However, there was a change in the N1s of the spent NC-900 catalyst. A new N-O bonding was formed at 402.8 eV (Fig. S8; ESI).52 Besides, the N-Q species dramatically decreased to 12.8%, compared to 24.84% in the fresh catalyst (Table S1) this causes the deactivation of the catalyst leading to decreasing catalytic activity.





Effect of biomass-derived furan and catalyst synthesized from the different carbon and nitrogen sources

To extend the application of this study to various biomassderived furan molecules, including furan, furfural, HMF, 2-furoic acid, and FDCA have been used as a substrate to produce MA over NC-900 catalyst under acid-free condition. As shown in Table 2, the furan compounds without a functional group and with either aldehyde or hydroxyl functional groups exhibited a 100% conversion at 80 °C within 5 h (Table 2, entry 1-3). Meanwhile, the furan compounds with an acid functional group showed lower conversion, which is in the range from 72-84% (Table 2, entry 4-5). Furthermore, MA yield was observed to be 41%, 28%, 38%, 40%, and 61% for furan, HMF, 2-furoic acid, FDCA, and furfural, respectively. This result indicates that the functional groups present on the furan ring significantly affects the catalyst reactivity for the catalytic oxidation of furan compounds into MA.

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 Table 2: The oxidation of biomass-derived furans to MA over NC-900

 catalyst



Reaction condition: Reactant (1 mmol), NC-900 catalyst (50 mg), water 5 mL, H_2O_2 5. mL (35 wt%), time 5h, temperature 80 $^{\circ}C$.





Further, we compared the effect of various N-doped carbon catalysts that were synthesized from the different carbon and nitrogen sources, such as ZIF-8 (ZIF-8-derived NC), melamine (melamine-derived $g-C_3N_4$), and chitosan-combined urea (biomass-derived NC). The melamine-derived $g-C_3N_4$ and biomass-derived NC were synthesized similar to the previously reported methods.^{34, 35} Further, these catalysts were characterized using XPS analysis to understand the type of nitrogen species (Fig. S9; ESI). As shown in Fig. 7, when the

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catalytic activity of melamine-derived $g-C_3N_4$ and biomassderived NC sample was tested for furfural oxidation, the results showed high furfural conversion (98% with biomass-derived NC and 100 with melamine-derived g-C₃N₄ catalyst). However, the melamine-derived g-C₃N₄ (20% MA) and biomass-derived NC catalyst (18% MA) exhibited a low MA yield. Whereas, the ZIF-8-derived NC showed higher MA yield (61%) under similar reaction conditions, indicating that the ZIF-8-derived NC (NC-900) is a highly selective and active catalyst for furfural oxidation into MA due to the higher content of graphitic nitrogen (N-Q) in the structure of ZIF-8-derived NC catalyst. From the results of the XPS analysis of g-C₃N₄ and biomassderived NC catalysts (Fig. S9; ESI), it can be seen that the N-Q species (graphitic N) present in g-C₃N₄ and biomass-derived NC catalyst is only 1.85% and 4.71%, which are lower than the N-Q species in ZIF-8-derived NC-900 catalyst (24.84%), this again confirms that the N-Q species of NC-900 catalyst playing an important role in the selective oxidation of furfural to MA. This comparison study showed that the ZIF-8-derived NC exhibited the high catalytic performance in the oxidation of furfural to MA compared to the g-C₃N₄ and biomass-derived NC. Further, The NC-900 catalyst is capable of converting a variety of biomassderived furan compounds to MA under acid-free condition, indicating the versatility and excellent applicability of the NCbased catalytic system.

Conclusions

Herein we report the catalytic oxidation of furfural into MA using an N-doped carbon catalyst in H₂O₂ liquid oxidant under the acid-free condition for the first time. The synthesized ZIF-8derived NC-900 catalyst shows a high percentage of graphitic nitrogen (24.84%), which exhibited high selectivity in the furfural oxidation to MA. The effect of various reaction parameters such as H₂O₂ concentrations, solvent effect, temperature and time effect was systematically studied in detail. A high yield of MA (61%) could be achieved at 80 °C in 5 h in the presence of NC-900 as catalyst and H_2O_2 as oxidant, respectively. We demonstrated with the XPS characterization that the graphitic nitrogen (N-Q species) is key active sites for catalytic oxidation of furfural into MA. Besides, the kinetic study showed that the furfural oxidation into MA over N-doped carbon catalyst was proceeding through the formation of 5hydroxy-furan-2(5H)-one as the main intermediate product, this shows that reaction happens through B pathway. A comparison of catalytic activity of N-doped carbon catalysts, including g-C₃N₄, biomass-derived NC, and ZIF-8-derived NC-900, suggested that the ZIF-8-derived NC exhibited the highest catalytic performance in the oxidation of furfural to MA, compared to the g-C₃N₄ and biomass-derived NC. We believe that this work can find potential applications for several biomass conversions under acid-free conditions.

Conflicts of interest

There are no conflicts of interest.

Acknowledgements

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Graphical Abstract

Oxidation of biomass-derived furans to maleic acid over nitrogen-doped carbon catalysts under the acid-free condition



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We report an acid-free effective furfural-to-MA conversion system using nitrogen-doped carbon catalyst and H_2O_2 oxidant.