The effect of Br- and alkali in enhancing the oxidation of furfural to maleic acid with hydrogen peroxide

Tao Yang [a], Wenzhi Li [a,b,*], Ajibola T. Ogunbiyi [a]

[a] *Laboratory of Basic Research in Biomass Conversion and Utilization, Department of Thermal Science and Energy Engineering, University of Science and Technology of China, Hefei, 230026, PR China*
[b] *Institute of Energy, Hefei Comprehensive National Science Center, Hefei, 230031, PR China*

ABSTRACT

This study was focused on investigating a novel catalytic system for the selective conversion of furfural to maleic acid (MA) in an aqueous system with hydrogen peroxide as an oxidant. A series of experiments that study the impacts of catalyst species, furfural concentration, catalyst dosage, reaction temperature, residue time, hydrogen peroxide concentration, excess water content, and solvent types on the oxidation of furfural to MA was carried out. The results showed that the co-existence of Br- and alkali sites might play a vital role in furfural oxidation, which could improve the MA yield remarkably. Under 90 °C for 3 h, 72.4 % MA yield was obtained with KOH and KBr as co-catalyst in an aqueous phase. Moreover, a possible reaction pathway of furfural oxidation was proposed on the basis of our reaction system.

1. Introduction

Maleic acid (MA), as one of the essential C_4 intermediates in the chemical industry, is involved in the synthesis of unsaturated polyester resins, vinyl copolymers, agricultural chemicals, surface coatings, and pharmaceuticals [1]. Currently, MA is needed industrially about 1 800 000 tons/year, which is produced mainly via the catalytic oxidation of petroleum-derived feedstock such as butane, butadiene, and benzene [2, 3]. However, with the depletion of petroleum feedstock and increasing environmental concerns, some researchers have paid much attention to developing new and renewable biomass-derived chemicals such as levulinic acid, 5-hydroxymethylfurfural, and furfural, to prepare MA in the past few years [4–8]. Among these biomass-derived platform chemicals, furfural has attracted more and more attention because furfural is a bulk industrial feedstock produced from lignocellulosic biomass at a rate of ca. 300 kilotons per year [9–13].

Various alternative and renewable furfural oxidation routes have been reported for MA production, particularly those that employed hydrogen peroxide (H_2O_2) as an oxidant. During these oxidation processes, heterogeneous and homogeneous catalytic systems have been developed for MA production [14]. The heterogeneous catalysts can be recovered easily from reaction system, however, the reaction efficacy is

relatively low which generally needed longer reaction time to obtain high MA yield. The homogeneous catalysts show the properties of high catalytic efficiency and high product selectivity, while there still remained problems such a recovery and recycling of catalysts. For example, in the field of heterogeneous catalysis, M. López Granados et al. reported that titanium silicalite (TS-1) could selectively oxidize furfural to MA with an 80 % yield under 50 °C, 28 h [15]. They also explored TS-1 deactivation, and the reasons were attributed to Ti leaching and heavy products deposition on the catalyst [16]. Then, by using γ-valerolactone as a solvent, the deactivation of catalysts can be suppressed [17]. Furthermore, several catalysts such as heteropoly acid, sulfonated resin, and carbon-based solid acid catalysts have also been reported for furfural oxidation [18–21]. In the homogeneous catalytic field, various novel reaction systems have also been investigated, which showed higher catalytic activities than heterogeneous catalysts. For example, Araji et al. used betaine hydrochloride as a catalyst to achieve a more than 90 % total yield of MA and fumaric acid (FA) [22]. Zhang et al. found that MA could be efficiently produced from furfural with formic acid as both a catalyst and solvent [23]. The authors proposed that carboxylic acids could be oxidized to organic peracids. The latter may play a vital role in the oxidation of furfural to MA [23,24]. Furthermore, inspired by a previous report, Yan et al. developed the

deep eutectic solvent (DES) as a solvent and catalyst, which consisted of choline chloride and oxalic acid, to obtain a 95.7 % total yield of MA and FA [25]. Different from the above reports, Zhu et al. used an alkali catalyst to investigate the effect of Mg(OH)$_2$ on furfural oxidation, which showed that the selectivity of 2(5 H)-furanone (FRO) and succinic acid (SA) could be enhanced by the presence of an alkali [26]. The author proposed that the OH$^-$ can facilitate the attack of the carbon in $-HC = O$ by HOO$^-$, which is beneficial for the formation of FRO and SA. As demonstrated, it has shown that the currently reported catalysts for MA production have not reflected the obvious similar properties because various types of catalysts (e.g., TS-1, organic acid, Mg(OH)$_2$) have been used during furfural oxidation. Furthermore, some studies have reported that an alkali presence could remarkably improve formic acid yield during the oxidation of glucose. For example, Jin et al. used KOH as a catalyst and H$_2$O$_2$ as an oxidant to convert glucose to formic acid, and a 75 % yield was obtained under 250 °C [27]. Wang et al. found that LiOH showed excellent catalytic activity for glucose conversion at room temperature with a 91.3 % formic acid yield [28]. According to the above reports, the presence of a base may be beneficial for accelerating the generation of HOO$^-$, hydroxyl, or superoxide ion species from H$_2$O$_2$, which could play a vital role in promoting the oxidation of furfural's carbonyl group. Thus, various types of alkali were used to investigate its possible effect in the furfural oxidation process. Furthermore, considering the diverse products in a single Mg(OH)$_2$ system and the positive effect of bromide for carboxy groups formation in previous reports, the bromide salts would also be added into the reaction system [29,30].

In this regard, the study was focused on a novel catalytic system for MA production from furfural oxidation with H$_2$O$_2$ as an oxidant, catalyzed by alkali and a Br-containing salt. A series of alkali species and various bromide-containing compounds were used as catalysts to explore the possible activity sites during the oxidation of furfural to MA. Furthermore, the effects of reaction time, temperature, catalyst contents, excess of water contents, H$_2$O$_2$/furfural concentration, and solvent types on the yield of MA were investigated systematically. Moreover, a possible reaction pathway was proposed based on these results. In conclusion, this study provides a novel and highly selective route to transform furfural to MA (Scheme 1).

2. Experimental

2.1. Materials

Furfural (99 %), 5-hydroxymethylfurfural (5-HMF, 98 %), 2(5 H)-furanone (FRO, 98 %), furoic acid (98 %), maleic acid (99 %), succinic acid (99 %), fumaric acid (98 %), lithium bromide (LiBr), and butyrrolactone (GBL) were purchased from Aladdin. (Shanghai, China). Potassium bromide (KBr), ammonium bromide (NH$_4$Br), sodium bromide (NaBr), potassium hydroxide (KOH), sodium hydroxide (NaOH), ammonia (NH$_3$·H$_2$O), potassium chloride (KCl), potassium nitrate (KNO$_3$), formic acid (FA), 1,4-dioxane, γ-valerolactone (GVL), hydrogen peroxide (H$_2$O$_2$, 30 %), sulphuric acid (98 %, H$_2$SO$_4$), and dimethyl sulfoxide (DMSO) were supplied by Sinopharm Chemical Co., Ltd. (Shanghai, China).
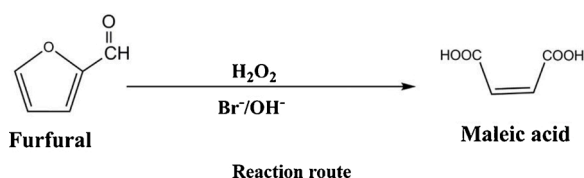
Scheme 1. Conversion of furfural to MA with Br$^-$/OH$^-$ in the presence of H$_2$O$_2$.

2.2. Experimental procedure

All catalytic oxidation reactions were conducted in a 15 ml thick-walled glass tube. Typically, 1 mmol furfural, 0.5 mmol KBr, 0.5 mmol mg KOH, 2 ml distilled water (DIW), and 1 ml H$_2$O$_2$ were added into the glass tube. Then the tube was heated in a preheated oil bath with magnetic stirring. After the specified reaction time elapsed, the tube was put in flowing water to end the reaction. Finally, the resultant products were stored in a 4 °C refrigerator for further analysis.

2.3. Product analysis

The quantitative analysis of MA, SA, FRO, and FA were determined by high-performance liquid chromatography (HPLC, Waters 515 pump), which has a HPX-87H column (Bio-Rad, USA) and a differential refractive index detector (Waters 2414). The column and detector temperature was set at 63 and 50 °C, respectively. Furthermore, a 5 mM H$_2$SO$_4$ solution was chosen as the mobile phase, and the flow rate was controlled at 0.6 mL/min.

The substrates, such as furfural and 5-HMF, were performed by HPLC equipped with a Symmetry-C18 column (30 °C) and an Ultraviolet Detector (Waters 2489) (detector wavelength 280 nm). Methanol and water (2/3, v/v) were used as mobile phase with a 0.4 mL/min flow rate.

The product yields were calculated by the external standard curves and the detailed information was added in the support information.

$$\text{Yield of product (mol\%)} = \frac{moles\ of\ product\ produced}{moles\ of\ starting\ substrate} \times 100\%$$

Product = MA, SA or FRO
Substrate = furfural, 5-HMF or furoic acid

3. Results and discussion

3.1. Influence of catalyst species on furfural oxidation experimental

In previous reports, Zhu et al. used Mg(OH)$_2$ as a catalyst, and they found that there was a synergy between Mg(OH)$_2$ and H$_2$O$_2$ in enhancing the yield of FRO and SA [26]. Furthermore, inspired by the high yield of formic acid from glucose catalyzed by KOH and LiOH [27, 28]. Therefore, KOH and NaOH were preliminarily used as catalysts in this study to investigate the effect of an alkali on furfural oxidation. When KOH and NaOH were added into the reaction system, three main products (MA, SA, FRO) were detected, which indicated that furfural oxidation with H$_2$O$_2$ as an oxidant and a base as a catalyst showed a lack of selectivity. Furthermore, Yan et al. have reported a new chemical route to produce terephthalic acid from corn-stover-derived lignin oil with Co-Mn-Br system and we wonder if the presence of KBr would be beneficial for the formation of carboxy groups on the furfural oxidation. Interestingly, when KBr was added into the reaction system, only MA was detected without the formation of SA and FRO, implying that the presence of KBr could inhibit the formation of SA and PRO. Considering the alkali role in promoting H$_2$O$_2$ activation, we then added KBr and KOH simultaneously into the reaction system. It was surprising that the MA yield could be improved to 64.3 % without SA and FRO. Thus, we guessed that halogen might play a vital role in enhancing MA selectivity. However, when KCl replaced KBr, 41.2 % MA, 24.2 % SA, and 10.4 % FRO yield were obtained, suggesting that the Cl$^-$ could not keep MA selectivity. Thus, it was proposed that the inhibition of SA and FRO formation may be ascribed to the effect of Br$^-$. Therefore, NaBr, NH$_4$Br, LiBr, and CaBr$_2$ were used as catalysts to verify our hypothesis, which gave 29.9 %, 27.7 %, 28.2 %, and 27.7 % MA yield, respectively. Similarly, SA and FRO could not be produced with these Br-containing catalysts. Furthermore, the MA yield also maintained similar results of about 30 %.

Furthermore, to investigate the role of alkali, KOH was added into

the above four types of Br-containing catalysts, and the MA yield improved to 64.6 %, 61.6 %, 63.1 %, and 54.3 % (Table 1, entries 11–14), respectively. Therefore, the high MA yield may be attributed to the role of Br^- and OH^-. Moreover, to exclude the effect of K^+ on the catalytic process, NH_4Br-NH_4OH (Table S1, entry 1) and LiBr-LiOH (Table S1, entry 2) were also used as catalysts, and 61.8 % and 59.8 % MA yields, respectively, were achieved in these conditions, which proved that the K^+ is not the crucial activity species for enhancing MA selectivity. To determine if there was any synergistic effect between other types of alkali and KBr, we also tested some common bases such as $NaHCO_3$, K_2CO_3, Na_2CO_3 (Table S1, entries 4–6). There were also no SA and FRO with the presence of these catalysts, but the yields of MA changed slightly with varying types of base precursors. Obviously, the yield of MA improved up to 63.9 % for $NaHCO_3$, 62.6 % for K_2CO_3, and 67.8 % for Na_2CO_3 added, while only 27.5 % of MA yield was obtained with only KBr as a catalyst, suggesting that the introduction of a strong or weak alkali may have a synergistic effect with Br^-. In conclusion, the results demonstrated that the presence of Br^- and alkali sites played a vital role in enhancing MA yield from furfural.

3.2. Furfural oxidation under varying substrate concentrations and catalyst contents

As we all know, high furfural concentrations are vital to enhance the industrial economic benefits of MA production. Thus, the effect of the initial furfural concentration (0.5−3 mmol) on MA production in reactions catalyzed by KBr-KOH was investigated, and the results are listed in Table 2. The MA yields are 66.3 %, 67.4 %, 51.5 %, and 37.9 % with 0.5, 1, 2, and 3 mmol furfural, respectively. According to the above results, increasing furfural contents from 0.5 to 3 mmol harmed the MA yield. We guessed that the low MA yield might be caused by the lack of H_2O_2 oxidant. Thus, an additional H_2O_2 was added to the reaction system. Under the conditions of 2 mmol furfural substrate, the MA yield increased to 61.4 % (Table 2, entry 5) and 63.0 % (Table 2, entry 6) with the increase of H_2O_2 to 2 ml and 3 mL, respectively. Similarly, when the 3 mmol furfural was used as a substrate, the MA yield increased to 58.8 % (Table 2, entry 7) and 64.8 % (Table 2, entry 8) with the increase of H_2O_2 to 2 ml and 3 mL. Therefore, with the further addition of furfural, the MA yield mainly depended on the amount of excess H_2O_2 added.

Besides furfural concentration, the catalyst dosage also has economic importance in the industrial production of MA, therefore, the effect of catalyst contents on catalytic properties was studied in detail. As shown in **Fig. S1**, the yield of MA increased from 53.0% to 72.2% as the KOH contents increased from 0.25 to 1.0 mmol with a constant KBr contents of 0.5 mmol, and the same phenomenon could be also observed with the constant KBr of 0.75 or 1.0 mmol. The best MA yield can be achieved with 0.5 mmol KBr and 0.75 mmol KOH. Furthermore, as the KBr

Table 1
Furfural oxidation using various catalysts.

Entry	catalyst	MA yield (%)	SA yield (%)	FRO yield (%)
1	blank	24.5	24.0	20.3
2	KOH	27.6	22.9	14.6
3	NaOH	29.8	21.3	15.9
4	KBr	27.5	–	–
5	KOH/KBr	64.3	–	–
6	KOH/KCl	41.2	24.2	10.4
7	NaBr	29.9	–	–
8	NH_4Br	27.7	–	–
9	LiBr	28.2	–	–
10	$CaBr_2$	27.7	–	–
11	KOH/NaBr	64.6	–	–
12	KOH/NH_4Br	61.6	–	–
13	KOH/LiBr	63.1	–	–
14	$KOH/CaBr_2$	54.3	–	–

Reaction conditions: catalyst 0.5 mmol (2–4, 7–10) or 0.5/0.5, mmol/mmol (5, 6, 11–14), furfural (1 mmol), DIW (2 mL), H_2O_2 (1 mL), 100 °C, 3 h.

Table 2
Furfural oxidation using different furfural concentrations.

Entry	Furfural (mmol)	H_2O_2 (mL)	MA yield (%)
1	0.5	1	66.3
2	1	1	67.4
3	2	1	51.5
4	3	1	37.9
5	2	2	61.4
6	2	3	63.0
7	3	2	58.8
8	3	3	64.8

Reaction conditions: KBr (0.5 mmol), KOH (0.5 mmol), 2 ml DIW, 100 °C, 3 h.

content further increased to 0.75 and 1.0 mmol (with a constant KOH contents of 0.75 mmol), the MA yield slightly decreased to 67.8 % and 70.0 %, respectively. Thus, excessive amounts of catalyst would result in by-reactions such as condensation, producing by-products [17,31]. So, an optimum catalyst ratio of 0.5/0.75 (mmol/mmol) was used in our subsequent studies. Furthermore, interestingly, when the KBr/KOH was 0.05 and 0.1 mmol (Table 3, entry 1–2), 14.7 % and 7.1 % FRO yields were obtained besides the presence of MA, respectively. However, when FRO was used as a substrate, there was no MA formation, as shown in Table 4 (Entries 1, 2), implying that the formation of FRO and MA are parallel reactions in our reaction system. Under the above conditions, which suggested that either there were no sufficient activity sites for MA formation or there was a lack of enough Br^- for the inhibition of FRO formation. Thus, FRO can be completely inhibited only when the amounts of KBr and KOH reach a certain level.

3.3. The effects of reaction temperature and retention time on furfural oxidation to maleic acid

The effects of reaction temperature and residue time on the conversion of furfural to MA in a water-H_2O_2 system were investigated by conducting the experiments under 70–110 °C within a time range of 2–5 h. As shown in Fig. 1, both reaction temperature and time affect the MA yield. The catalytic reaction at 90, 100 and 110 °C gave high MA yields within only 2 h, quicker than that of 70 and 80 °C. The possible reason is that a higher reaction temperature could increase the transformation rate of H_2O_2 (evident by the bubbles formed at the end of the reaction), thereby promoting the oxidation of furfural. Under low reaction temperature (70, 80 °C), a longer reaction time of up to 5 h would favor MA formation. The optimal reaction temperature is 90 °C, and the highest MA yield reached was 72.4 % at 3 h, indicating that the KBr-KOH was efficient for such an oxidation reaction. Although higher reaction temperatures can reduce the reaction time, yield loss reactions might occur since the MA yield decreased when the temperature increased to 100 and 110 °C.

3.4. The effect of H_2O_2/furfural ratios and water contents on furfural oxidation

As described earlier, H_2O_2 plays a vital role in the conversion of furfural to MA. Thus, the effect of H_2O_2 concentration on MA formation was investigated by varying the H_2O_2/furfural mole ratio from 1.7 to

Table 3
Effect of catalyst concentrations on the furfural oxidation.

Entry	KBr/KOH (mmol-mmol)	MA yield (%)	FRO yield (%)
1	0.05−0.05	38.1	14.7
2	0.1−0.1	51.9	7.1
3	0.25−0.25	58.7	–
4	0.5−0.5	67.4	–
5	0.75−0.75	67.8	–
6	1.0−1.0	67.1	–

Reaction conditions: catalyst (KBr-KOH), 2 mL DIW, H_2O_2 (1 mL), 100 °C, 3 h.

Table 4
Oxidation of various substituted furan compounds.

Entry	Substrate	Catalyst	MA yield (%)	SA yield (%)	FRO yield (%)
1	FRO	KBr	–	–	73.3[a]
2	FRO	KBr-KOH	–	–	–
3	Furoic acid	KBr	28.9	–	–
4	Furoic acid	KBr-KOH	87.1	–	–

Reaction conditions: substrate (1 mmol), DIW (2 mL), H_2O_2 (1 mL), 100 °C, 3 h.
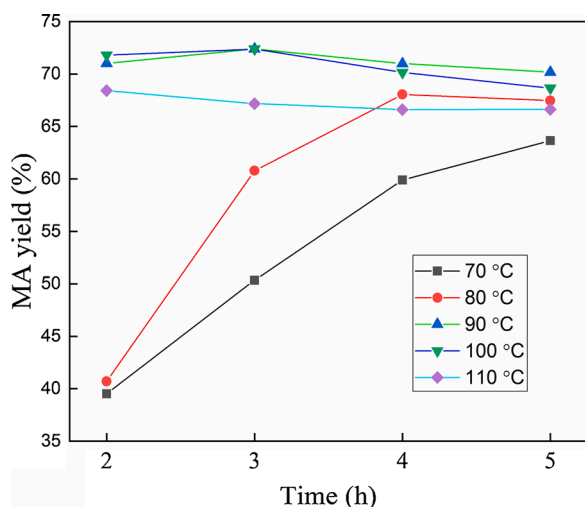[a] the remained FRO.

Fig. 1. Effect of the reaction temperature and time on the oxidation of furfural in a KBr-KOH system. Reaction conditions: Furfural (1 mmol), DIW (2 mL), KBr/KOH (0.5/0.75 mmol/mol), H_2O_2 (1 mL).

10.2, and the results are shown in Fig. 2A. The increase in the mole ratio of H_2O_2 to furfural resulted in the variation of the maleic acid yield. When the mole ratio increased from 1.7 to 5.1, the MA yield increased from 31.0% to 71.6%, and a slight increase to 72.4 % with the mole ratio up to 6.8. While the MA yield are 71.7 % and 72.6 % respectively with the mole ratio reaching to 8.5 and 10.1. According to previous reports [15], the stoichiometric amount of H_2O_2 needed for transforming furfural to MA is 3; however, a higher H_2O_2/furfural mole ratio was required to supplement the underside consumption reactions of H_2O_2. It should be mentioned here that the use of ratios higher than 6.8 did not give obvious further increase in MA yield, suggesting that the optimum
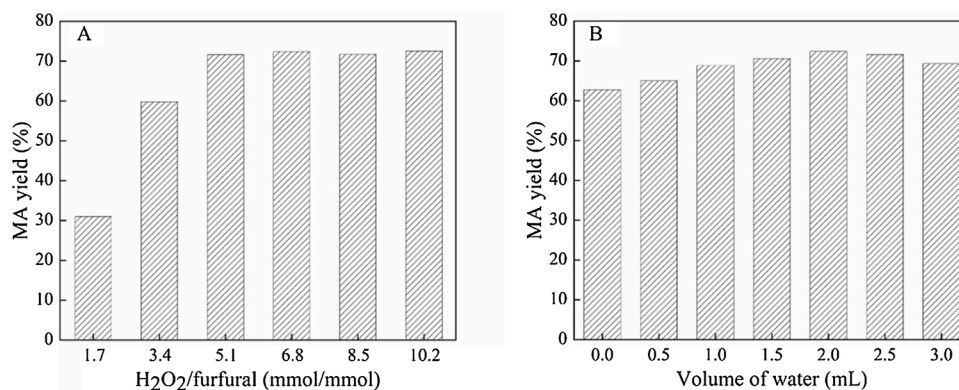
mole ratio of H_2O_2 to furfural was 6.8. Therefore, this optimum ratio was used for further investigation.

The amount of excess water is also a vital parameter influencing the reaction [25], and the results of this investigation are shown in Fig. 2B. The MA yield increased with the increase of excess water up to 2 mL. However, as the amount of excess water increased further to 3 mL, the yield of MA has a slight decrease, suggesting that proper water content is beneficial for MA production, as excess water may affect H_2O_2 and the catalyst properties. The similar results have been explored in previous reports, for example, the MA yield decreased remarkably with additional water adding into formic acid or deep eutectic solvent catalytic system [23,25]. Moreover, when no excess water was added to the reaction system, the MA yield only reached to 62.8 %. In this regard, water is essential, and suitable water content would also play a crucial role in the whole process of furfural oxidation.

3.5. Effect of solvent types on the production of maleic acid

Solvent types may also play an important role in furfural oxidation to MA because it can influence the dispersion of furfural and MA's distribution and isolation. The previous report has demonstrated that solvents such as GVL can improve the di-acids yield with TS-1 as a catalyst. Thus, to explore the effect of solvent on furfural oxidation reaction, various common solvents such as water, GVL, GBL, 1, 4-dioxane, and DMSO
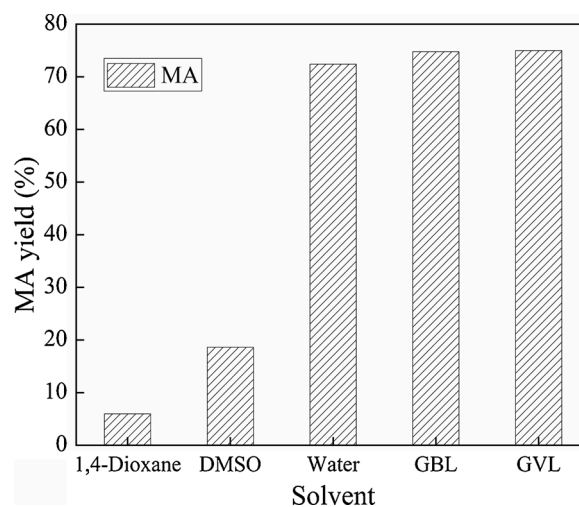

Fig. 3. Effect of solvent types on furfural oxidation.
Reaction conditions: furfural (1 mmol), solvent (2 mL), KBr/KOH (0.5 /0.75 mmol), H_2O_2 (1 mL), 100 °C, 3 h.

Fig. 2. Effect of H_2O_2/furfural ratio (A) and excess water on furfural oxidation (B).
Reaction conditions: (A) 1 mmol furfural, 0.5 mmol KBr, 0.75 mmol KOH, 2 mL DIW, 0.25–1.5 mL H_2O_2, 100 °C, 3 h; (B) Furfural (1 mmol), excess water (0–3.5 mL), KBr/KOH (0.5 mmol/0.75 mmol), H_2O_2 (1 mL), 100 °C, 3 h.

were investigated. As shown in Fig. 3, when 1, 4-dioxane and DMSO were used as solvents, the MA yield was very low. Similar to previous reports, the lactone solvents can be a good solvent for this reaction process. Specifically, the MA yield is in the order of GVL (74.9 %)> GBL (74.7 %) > water (72.4 %) > DMSO (18.6 %) > 1, 4-dioxane (5.9 %). Higher MA yields are obtained with lactone as an organic solvent, which could be attributed to the good solvent effect for reducing by-reactions. Compared with GVL and GBL, the aqueous system showed a moderate MA yield of 72.4 %. The nature of water as a green, inexpensive, and abundant solvent makes its use in future industrial production promising.

3.6. Possible reaction pathway

During the experimental process, by comparing with blank experiment or KBr as a catalyst, the remaining H_2O_2 concentrations on the spectrum of HPLC decreased obviously with KOH addition to the catalytic system, which implied that KOH showed high activity for H_2O_2 transformation. Furthermore, in Table 1, to reveal whether Br^- is the real active site in converting furfural to maleic acid, LiBr-LiOH were used as catalysts to carry out the furfural oxidation reaction without the presence of K^+. It is fully confirmed that MA's high selectivity is attributed to Br- and OH- participation. Thus, a possible reaction pathway is proposed for the oxidation of furfural to MA based on Br- and a base catalyst.

Generally, there are two main reaction pathways for furfural oxidation to MA in the presence of H_2O_2. The first pathway starts with Baeyer-Villiger oxidation of furfural to furanol formate ester, which can be hydrolyzed to formic acid and 2-hydroxyfuran. Then the 2-hydroxyfuran can isomerize to furan-2(5 H), which can be oxidized to MA further. As mentioned before, when FRO was used as a raw substrate, there was no MA formation (Table 4, entry 2), suggesting that the FRO was not the intermediate during the MA formation process with KBr/KOH as a catalyst. Thus, the reaction pathway with FRO as the intermediate would be discarded for our reaction system. Furthermore, FRO was detected in section 3.2 with relatively low catalyst contents (0.05 or 0.1 mmol). FRO formation was inhibited at higher MA yield as the catalyst content increased further, demonstrating that the FRO and MA formation may be parallel reactions. The second pathway involves 2-furoic acid, converted to furan via decarboxylation that can be oxidized to maleic acid by H_2O_2. Because 2-furoic acid was observed in our control reactions, and 2-furoic was used as a starting material, 87.1

% MA yield was achieved (Table 4, entry 4). Thus, it is likely that our reaction proceeds through the 2-furoic acid route. Hence, a possible reaction pathway was proposed for the whole catalytic reaction process of furfural oxidation in the presence of Br and a base catalyst, and this is shown in Scheme 2.

According to previous reports, an alkali presence may result in the ionization of H_2O_2 to produce HOO^- species, and the HOO^- can react with furfural's carbonyl group due to the nucleophilic addition reaction [26,32]. This step leads to the formation of furfural peroxide, which is not stable and subsequently suffers a Baeyer-Villiger reaction yielding 2-formyloxyfuran. The latter was rapidly hydrolysed to 2-hydroxyfuran in an aqueous solution releasing formic acid. Actually, this step represents the loss of a carbon atom from furfural (C5) to form a C4 species. In general, 2-hydroxyfuran can keep a keto-enol tautomeric equilibrium with 5-furanones and 3-furanones. The latter can be oxidized with H_2O_2 to succinic acid further in the blank reaction. However, the SA and FRO can be inhibited in our system by Br- and alkali's presence. Then, a different reaction pathway was proposed for this specific case. The 2-hydroxyfuran was oxidized to species **1** through electron transfer, which was attacked by Br^- to from species **2**. The latter could be easily transformed into maleic dialdehyde because Br^- is a good leaving group. Lastly, maleic dialdehyde can be further oxidized to MA. Herein, it was demonstrated that the synergistic effect between Br^- and OH^- active sites in the catalytic system is responsible for controlling MA's catalytic selectivity.

4. Conclusions

An efficient and novel reaction route was developed to convert furfural into maleic acid. As demonstrated, the product distribution was correlated with the catalyst properties, and the presence of bromide salts and alkali improved the MA yield remarkably. Based on the detailed studies of the effects of reaction temperature, time, furfural contents, H_2O_2 concentration, water volume, and catalyst contents, 72.4 % MA yield was achieved under optimized reaction conditions. It was demonstrated that the high MA yield might be ascribed to the synergistic effect between Br^- and alkali; specifically, the alkali may play a vital role in H_2O_2 activation, and the bromide anions could inhibit the formation of SA and FRO. Furthermore, a possible reaction pathway was proposed based on the synergistic effect between Br^- and OH^-. In conclusion, the results may provide a new and green furfural conversion route to MA, which can further be a potential C_4 intermediate for
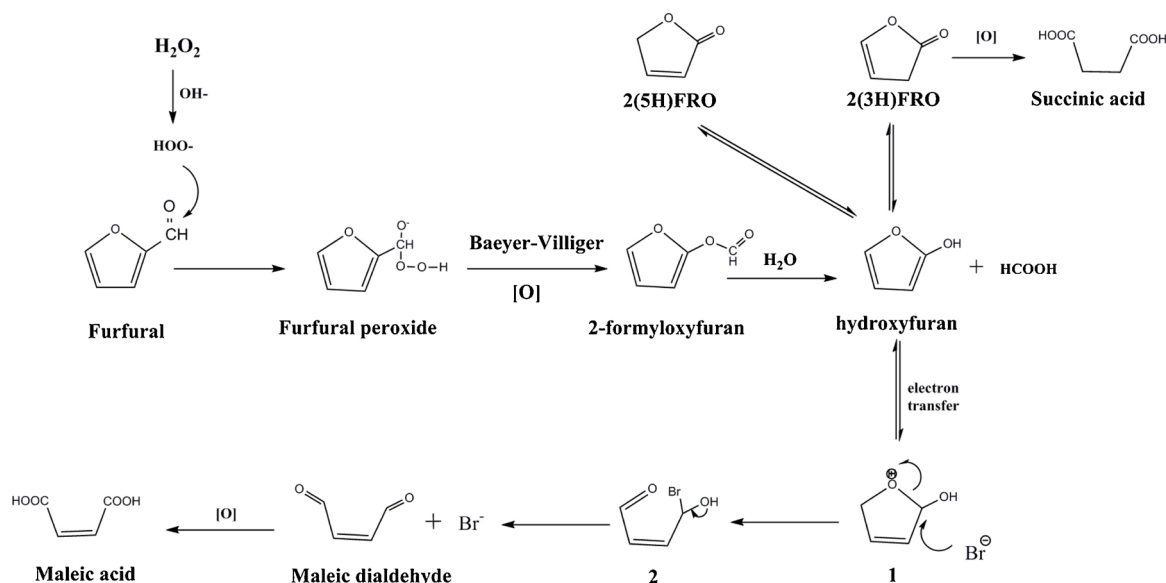
Scheme 2. Proposed reaction pathway for the oxidation of furfural with Br^- and alkali catalysts.

unsaturated polyester resins.

CRediT authorship contribution statement

Tao Yang: Conceptualization, Methodology, Formal analysis, Investigation, Resources, Data curation, Writing - original draft, Visualization, Project administration, Supervision. **Wenzhi Li:** Conceptualization, Validation, Data curation, Writing - review & editing, Project administration, Funding acquisition. **Ajibola T. Ogunbiyi:** Resources, Writing - review & editing.

Declaration of Competing Interest

The authors declare no conflict of interest.

Acknowledgements

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2021.111488.

References

[1] Y. Zhao, H. Xu, K. Wang, K. Lu, Y. Qu, L. Zhu, S. Wang, Enhanced furfural production from biomass and its derived carbohydrates in the renewable butanone–water solvent system, Sustain Energy & Fuels 3 (2019) 3208–3218.

[2] N. Alonso-Fagundez, M.L. Granados, R. Mariscal, M. Ojeda, Selective conversion of furfural to maleic anhydride and furan with VO(x)/Al(2)O(3) catalysts, Chem. Sus. Chem. 5 (2012) 1984–1990.

[3] N. Alonso-Fagúndez, M. Ojeda, R. Mariscal, J.L.G. Fierro, M. López Granados, M. nados, Gas phase oxidation of furfural to maleic anhydride on V2O5 /γ-Al2O3 catalysts: reaction conditions to slow down the deactivation, J. Catal. 348 (2017) 265–275.

[4] Z. Du, J. Ma, F. Wang, J. Liu, J. Xu, Oxidation of 5-hydroxymethylfurfural to maleic anhydride with molecular oxygen, Green Chem. 13 (2011) 554–557.

[5] H. Guo, G. Yin, Catalytic aerobic oxidation of renewable furfural with phosphomolybdic acid catalyst: an alternative route to maleic acid, J. Phys. Chem. C 115 (2011) 17516–17522.

[6] J. Lan, J. Lin, Z. Chen, G. Yin, Transformation of 5-hydroxymethylfurfural (HMF) to maleic anhydride by aerobic oxidation with heteropolyacid catalysts, ACS Catal. 5 (2015) 2035–2041.

[7] T. Soták, M. Hronec, M. Gál, E. Dobročka, J. Škriniarová, Aqueous-phase oxidation of furfural to maleic acid catalyzed by copper phosphate catalysts, Catal. Lett. 147 (2017) 2714–2723.

[8] R. Zhu, A. Chatzidimitriou, B. Liu, D.J. Kerwood, J.Q. Bond, Understanding the origin of maleic anhydride selectivity during the oxidative scission of levulinic acid, ACS Catal. 10 (2019) 1555–1565.

[9] J. Wu, X. Zhang, Q. Chen, L. Chen, Q. Liu, C. Wang, L. Ma, One-pot hydrogenation of furfural into tetrahydrofurfuryl alcohol under ambient conditions over PtNi alloy catalyst, Energy Fuels 34 (2020) 2178–2218.

[10] Z. Yi, H. Xu, D. Hu, K. Yan, Facile synthesis of supported Pd catalysts by chemical fluid deposition method for selective hydrogenation of biomass-derived furfural, J. Alloys Compd. 799 (2019) 59–65.

[11] Q. Liu, Q. Liu, X. Hu, Selective conversion of furfural into value-added chemical commodity in successive fixed-bed reactors, Catal. Commum. 135 (2020), 105836.

[12] C. Xu, E. Paone, D. Rodriguez-Padron, R. Luque, F. Mauriello, Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural, Chem. Soc. Rev. 49 (2020) 4273–4306.

[13] Z. Zhang, X. Hu, S. Zhang, Q. Liu, S. Hu, J. Xiang, Y. Wang, Y. Lu, Direct conversion of furan into levulinate esters via acid catalysis, Fuel 237 (2019) 263–275.

[14] P.L. Arias, J.A. Cecilia, I. Gandarias, J. Iglesias, M. López Granados, R. Mariscal, G. Morales, R. Moreno-Tost, P. Maireles-Torres, Dation of lignocellulosic platform molecules to value-added chemicals using heterogeneous catalytic technologies, Catal. Sci. Technol. 10 (2020) 2721–2757.

[15] N. Alonso-Fagúndez, I. Agirrezabal-Telleria, P.L. Arias, J.L.G. Fierro, R. Mariscal, M.L. Granados, Aqueous-phase catalytic oxidation of furfural with H2O2: high yield of maleic acid by using titanium silicalite-1, RSC Adv. 4 (2014) 54960–54972.

[16] A.C. Alba-Rubio, J.L.G. Fierro, L. León-Reina, R. Mariscal, J.A. Dumesic, M. López Granados, Oxidation of furfural in aqueous H2O2 catalysed by titanium silicalite: deactivation processes and role of extraframework Ti oxides, Appl. Catal. B 202 (2017) 269–280.

[17] Y. Rodenas, R. Mariscal, J.L.G. Fierro, D. Martín Alonso, J.A. Dumesic, M. López Granados, Improving the production of maleic acid from biomass: TS-1 catalysed aqueous phase oxidation of furfural in the presence of γ-valerolactone, Green Chem. 20 (2018) 2845–2856.

[18] H. Choudhary, S. Nishimura, K. Ebitani, Highly efficient aqueous oxidation of furfural to succinic acid using reusable heterogeneous acid catalyst with hydrogen peroxide, Chem. Lett. 41 (2012) 409–411.

[19] H. Choudhary, S. Nishimura, K. Ebitani, Metal-free oxidative synthesis of succinic acid from biomass-derived furan compounds using a solid acid catalyst with hydrogen peroxide, Appl. Catal. A 458 (2013) 55–62.

[20] P. Maneechakr, S. Karnjanakom, Catalytic transformation of furfural into bio-based succinic acid via ultrasonic oxidation using β-cyclodextrin-SO3H carbon catalyst, Energy Convers. Manage. 154 (2017) 299–310.

[21] W. Zhu, F. Tao, S. Chen, M. Li, Y. Yang, G. Lv, Efficient oxidative transformation of furfural into succinic acid over acidic metal-Free graphene oxide, ACS Sustain. Chem. Eng. 7 (2018) 296–305.

[22] N. Araji, D.D. Madjinza, G. Chatel, A. Moores, F. Jérôme, K. De Oliveira Vigier, Synthesis of maleic and fumaric acids from furfural in the presence of betaine hydrochloride and hydrogen peroxide, Green Chem. 19 (2017) 98–101.

[23] X. Li, B. Ho, D.S.W. Lim, Y. Zhang, Highly efficient formic acid-mediated oxidation of renewable furfural to maleic acid with H2O2, Green Chem. 19 (2017) 914–918.

[24] X. Li, X. Lan, T. Wang, Selective oxidation of furfural in a bi-phasic system with homogeneous acid catalyst, Catal. Today 276 (2016) 97–104.

[25] Y. Ni, Z. Bi, H. Su, L. Yan, Deep eutectic solvent (DES) as both solvent and catalyst for oxidation of furfural to maleic acid and fumaric acid, Green Chem. 21 (2019) 1075–1079.

[26] X. Xiang, B. Zhang, G. Ding, J. Cui, H. Zheng, Y. Zhu, The effect of Mg(OH)2 on furfural oxidation with H2O2, Catal. Commun. 86 (2016) 41–45.

[27] F. Jin, J. Yun, G. Li, A. Kishita, K. Tohji, H. Enomoto, Hydrothermal conversion of carbohydrate biomass into formic acid at mild temperatures, Green Chem. 10 (2008) 612.

[28] C. Wang, X. Chen, M. Qi, J. Wu, G. Gözaydın, N. Yan, H. Zhong, F. Jin, Room temperature, near-quantitative conversion of glucose into formic acid, Green Chem. 21 (2019) 6089–6096.

[29] T. Yang, W. Li, Q. Liu, M. Su, T. Zhang, J. Ma, Synthesis of maleic acid from biomass-derived furfural in the presence of KBr/Graphitic carbon nitride (g-C3N4) catalyst and hydrogen peroxide, BioRes 14 (2019) 5025–5044.

[30] S. Song, J. Zhang, G. Gökalp, N. Yan, Production of terephthalic acid from corn stover lignin, Angew. Chem. Int. Ed. 58 (2019) 4934–4937.

[31] A.S. Dias, M. Pillinger, A.A. Valente, Mesoporous silica-supported 12-tungsto-phosphoric acid catalysts for the liquid phase dehydration of d-xylose, Microporous Mesoporous Mater. 94 (2006) 214–225.

[32] V.Ge. Kul'nevich, L.A. Badovskaya, Reactions of oxo-derivatives of furan with hydrogen peroxide and peroxy-acids, Russ. Chem. Rev. 44 (1975) 574.