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SUSTAINABLE
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REVIEW
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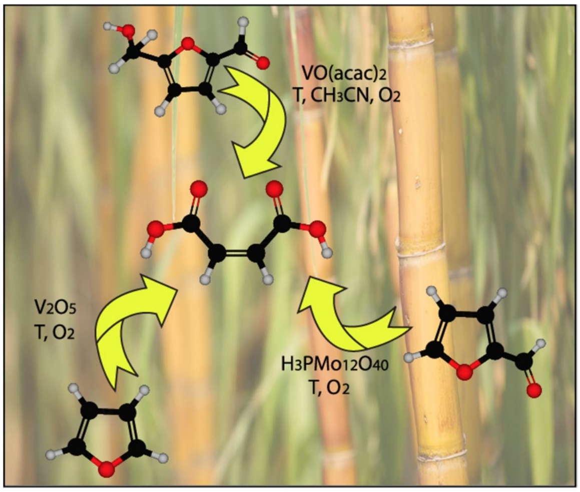
Recent developments in maleic acid synthesis from bio-based chemicals

Robert Wojcieszak[1*], Francesco Santarelli[1,2,3], Sébastien Paul[1,2], Franck Dumeignil[1,4], Fabrizio Cavani[3] and Renato V Gonçalves[5]

Abstract

This review paper presents the current state of the art on maleic acid synthesis from biomass-derived chemicals over homogeneous or heterogeneous catalysts. It is based on the most recent publications on the topic, which are discussed in details with respect to the observed catalytic performances. The recent developments and the technical drawbacks in the gas and the liquid phases are also reported. In addition, recent results on the mechanistic aspect are discussed giving insights into the probable reaction mechanisms depending on the starting molecule (furan, furfural and *5*-hydroxymethylfurfural).

Graphical abstract:



Keywords: Maleic acid, Heterogeneous catalysis, Furfural, Furan, HMF, Oxidation reaction, Nanomaterials

Background

Maleic acid (MA) and fumaric acid (FA) are very important chemical intermediates that find applications in nearly every field of industrial chemistry. Maleic acid is an important raw material used in the manufacture of lubricant additives, unsaturated polyester resins, surface coatings, plasticizers, copolymers and agricultural chemicals [1–5]. Fumaric acid is naturally present in many plants and its name originates from *Fumaria officinalis*, a climbing annual plant, from which it was first isolated [6]. It is used as a food acidulent and as a raw material

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in the manufacture of unsaturated polyester resins, quick setting inks, furniture lacquers, paper sizing chemicals, and aspartic acid [7, 8].

Maleic acid and fumaric acid are dicarboxylic acid isomers that have the same carbon skeleton. They both yield succinic acid (SA) by hydrogenation. Each can be converted to the identical anhydride by heat treatment, but maleic acid reacts much more rapidly. This, coupled with the fact that mild hydrolysis of maleic anhydride (MAnh) leads to maleic acid, is linked to the *cis* structure of maleic acid and to the *trans* structure of fumaric acid (Scheme 1). They contain two acid carbonyl groups and a double bond in the α,β position. These functional groups are very reactive, which makes the control of the selectivity of their synthesis reactions a key parameter.

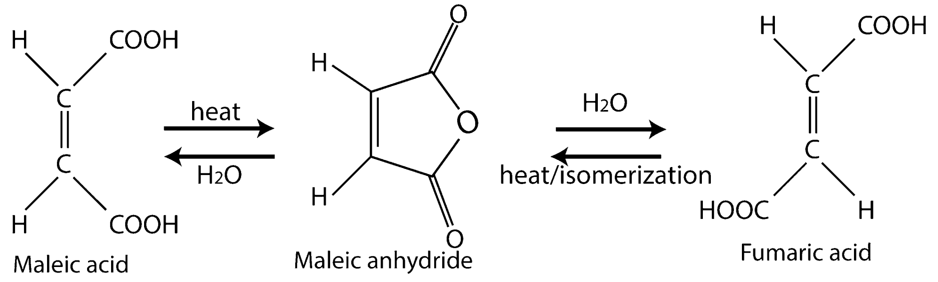
Historically, these two acids were first prepared in the 1830's, [9] but their commercial manufacture did not begin until almost one century later. Maleic acid was commercially available in 1928 and fumaric acid production began in 1932 using an acid-catalyzed isomerization of maleic acid process.

Maleic anhydride can be commercially produced by the vapor-phase oxidation of benzene or butene/butane using O_2 as an oxidant [10–15]. This later reaction is very exothermic and CO and CO_2 thus constitute the main by-products. The catalyst used in the production of maleic anhydride from butane is vanadium–phosphorus-oxide (VPO). There are several routes to prepare this catalyst, but the industrial way involves the reaction of vanadium (V) oxide and phosphoric acid to form vanadyl hydrogenophosphate, $VOHPO_4 \oplus 0.5H_2O$, which is then treated thermally to produce $(VO)_2P_2O_7$. The catalyst used for the conversion of benzene to maleic anhydride consists of supported vanadium oxide [16]. The vanadium oxide on the surface of the support is often modified with molybdenum oxides. The support is an inert oxide such as alumina or silica of a relatively low surface area. The conversion of benzene to maleic anhydride is a less complex oxidation than the conversion of butane, which enables obtaining very good conversions together with high selectivities [9].

Fumaric acid is generally produced by fermentation [17–20]. Many aspects such as the applied microbial strain and its morphology, the use of a neutralizing agent, and the applied feedstock play a crucial role in the fermentation process. This latter is very interesting because it involves CO_2 fixation. Indeed, it is known that the mechanism involving CO_2 fixation and catalyzed by pyruvate carboxylase enables obtaining higher yields in FA production. In case of the maximum theoretical yield, two moles of CO_2 could be fixed per mole of glucose consumed [19].

The quest for sustainable and environmentally benign sources of energy and, more recently, of chemicals has attracted much attention in the recent years [6]. The production and the use of chemicals and fuels from biomass [9, 21–23] seem to be an ideal solution to tackle environmental issues and fossil resources progressive depletion, if correct measures are taken. In that context, biomass-derived platform molecules, such as maleic acid, fumaric acid or maleic anhydride have been identified as top value-added chemicals. Therefore, a highly effective method to produce these dicarboxylic acids from biomass is necessary. Moreover, from the industrial application point of view, this method should be simple and environmentally friendly. In this context, heterogeneous catalysis could bring new economic and environmental solutions. Indeed, nowadays, new synthesis techniques permit to control the morphology and physical and chemical properties of the catalysts. This yields in higher conversion rates and selectivities. In some cases they are as good as for the enzymatic or homogeneous catalysts. As a matter of fact, a better understanding of catalytic nanomaterials is essential for the synthesis of fine chemicals.

In this review, we present the current state of the art on maleic acid synthesis by upgrading biomass-derived molecules (furfural and 5-hydroxymethylfurfural) using heterogeneous and homogeneous catalytic processes. This paper is based on the most recent publications, and we put emphasis on the factors that have to be considered to



Scheme 1 Chemical structures of maleic acid, fumaric acid and maleic anhydride.

understand the catalytic activity of the nanomaterials in maleic acid synthesis.

Platform molecules used for MA, FA and MAnh synthesis

Production of high value added chemicals from biomass sources remains one of the greatest contemporary challenges for heterogeneous catalysis. A very important point to be analyzed is related to the choice of the substrate and to its availability in the future. The major sources of this kind of raw material are agricultural residues and wastes, such as rice straw, wheat straw, wood (hardwood), byproducts left over from the corn milling process (corn strover), annual and perennial crops, waste paper and sweet sorghum. These raw materials comprise three types of main biopolymers: cellulose, hemicellulose, and lignin [24].

Due to its numerous advantages for growth and production, biomass raw materials has been identified as a suitable source of chemical energy for biofuels [25]. However, in order to synthesize fine chemicals of the desired size and properties, catalytic C–C bond formation is required. To this respect, *5*-hydroxymethylfurfural (HMF), furan and furfural obtained by transformation of carbohydrates, have been widely identified as useful platform molecules [26, 27]. The respective chemical structures of these molecules are represented in Scheme 2.

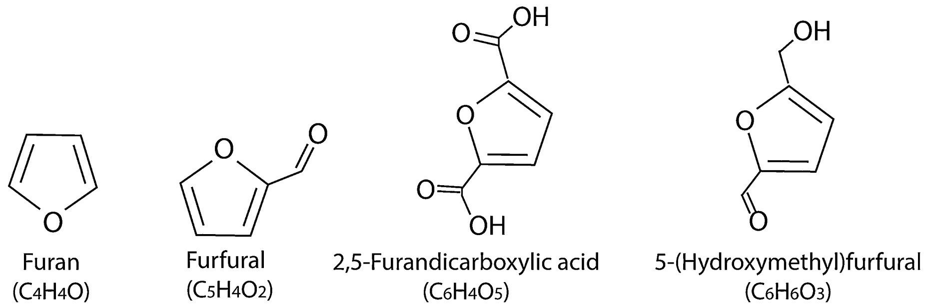
The list of the most important building block chemicals (platform molecules) that can be produced from sugars via biological or chemical conversions is now well established [28]. These building blocks can be subsequently converted to a number of high-value bio-based chemicals or materials. These molecules have multiple functional groups that possess the potential to be transformed into new families of useful molecules.

Other very important platform molecules are HMF and furfural. HMF is a versatile platform chemical. HMF could be easily transformed into maleic anhydride because it contains a furyl ring in its basic structure. This transformation could be achieved via oxidative C–C bond cleavage of HMF. Furfural is an important renewable, non-petroleum based, chemical feedstock. It could be easily transformed into furfuryl alcohol (FAlc), via hydrogenation, which is a very useful chemical intermediate [precursor of tetrahydrofurfuryl alcohol (THFA)]. It could be also transformed into maleic anhydride or maleic acid, via oxidation, as we will discuss later in the present paper. The by-product of furfural oxidation in gas phase is furan. This molecule is also one of the important intermediates in chemical industry. Moreover, as indicated below, furan is also the first intermediate in the mechanism of the furfural oxidation. Even if it cannot be produced directly from biomass (it can be produced from furfural) due to its presence in the reaction mechanism we have decide to include it into the present review.

Biomass feedstocks are highly reactive by nature, and, consequently, high temperature is normally not required to achieve their transformation. However, reactions carried out in the liquid phase increases the possibility of leaching issues. For this reason, rather than thermal stability, the new catalysts for biomass conversion should be designed so as to be resistant to leaching [29]. This is one of the most important challenges in liquid phase heterogeneous catalysis. However, taking into account the huge number of paper on leaching issues, we think that this subject needs a separate review. That is the reason why we do not discuss on leaching phenomenon in details in this work.

Liquid phase oxidation: homogeneous and heterogeneous catalysis

Guo and Yin [30] studied aerobic oxidation of furfural into maleic acid using phosphomolybdic acid catalysts. They performed the reaction in a biphasic aqueous/organic medium. The oxidation takes place in the aqueous phase and the organic phase plays the role of a reservoir, which gradually releases the substrate, which is unstable in the aqueous phase, through phase equilibrium. They studied



Scheme 2 Chemical structures of furan, furfural, 2,5-furandicarboxylic acid and *5*-hydroxymethylfurfural (HMF).

the influence of the co-solvent addition on the distribution of furfural between both phases, which influences its overall conversion. Without the organic co-solvent, the yield of maleic acid was 38.1% with 44.2% of selectivity, and the conversion of furfural was as high as 86.2%. Addition of an organic co-solvent generated a biphasic system, and improved the selectivity to maleic acid (up to 61% in the case of tetrachloroethane) with a concomitant reduction of the furfural conversion in most cases. The authors also studied the influence of the reaction temperature on catalytic activity and they found that when the reaction temperature was increased, the furfural conversion, the maleic acid yield, and the selectivity to maleic acid first increased, and at a temperature higher than 383 K, the furfural conversion and the maleic acid yield increased, but the selectivity to maleic acid then decreased. At 383 K, the conversion of furfural, the yield and selectivity to maleic acid were 50.3, 34.5, and 68.6%, respectively, whereas they were 87.6, 47, and 53.3% at 403 K. Moreover, at this latter temperature 3% of fumaric acid was observed, which reflects competitive polymerization (Figure 1).

Du et al. [31] studied the selective oxidation of HMF to maleic anhydride using $VO(acac)_2$ catalysts. They also observed a crucial role of the solvent in this reaction. 52% yield of MA was obtained in acetonitrile at 363 K, but a 14% yield of 2,5-diformylfuran (DFF) was also observed. Besides acetonitrile, acetic acid was preferred as a solvent for the formation of MA (50% MA yield). In contrast, MA yields of about 7% were observed in the case of *N*,*N*-dimethyl-formamide (DMF) and *α*,*α*,*α*-trifluorotoluene (TFT). The authors also observed that the reaction temperature strongly affected the oxidation process in terms of products distribution. When the reaction was performed at 343 K, the HMF conversion was no more than 50%. However, when the temperature was raised from 363 to 403 K, the yield of MA gradually decreased from 52 to 20% while the yield of DFF increased from 14 to 52%. Transition metals complexes such as $FeSO_4$, $CuSO_4$, $Mn(acac)_2$, $MoO_2(acac)_2$, $Co(acac)_2$ and $Co(OAc)_2$ studied by the authors in the same conditions were found much less effective for catalytic oxidation of HMF into MA, and the yield of MA was then <2%.

Quite similar results were observed in the oxidation of furfural in the presence of redox metal salt catalysts [32]. It was shown that copper acetate and iron sulfate enabled respectively 18.6 and 12.1% yields in the expected maleic acid. On the other hand, the catalysts based on other metal sources such as $Mn(OAc)_2$, $RuCl_3$ and $NiCl_2$ are substantially much less efficient for maleic acid formation. Interestingly, a $Pd(OAc)_2$ catalyst showed a 15.9% yield to furoic acid, while only traces of this compound

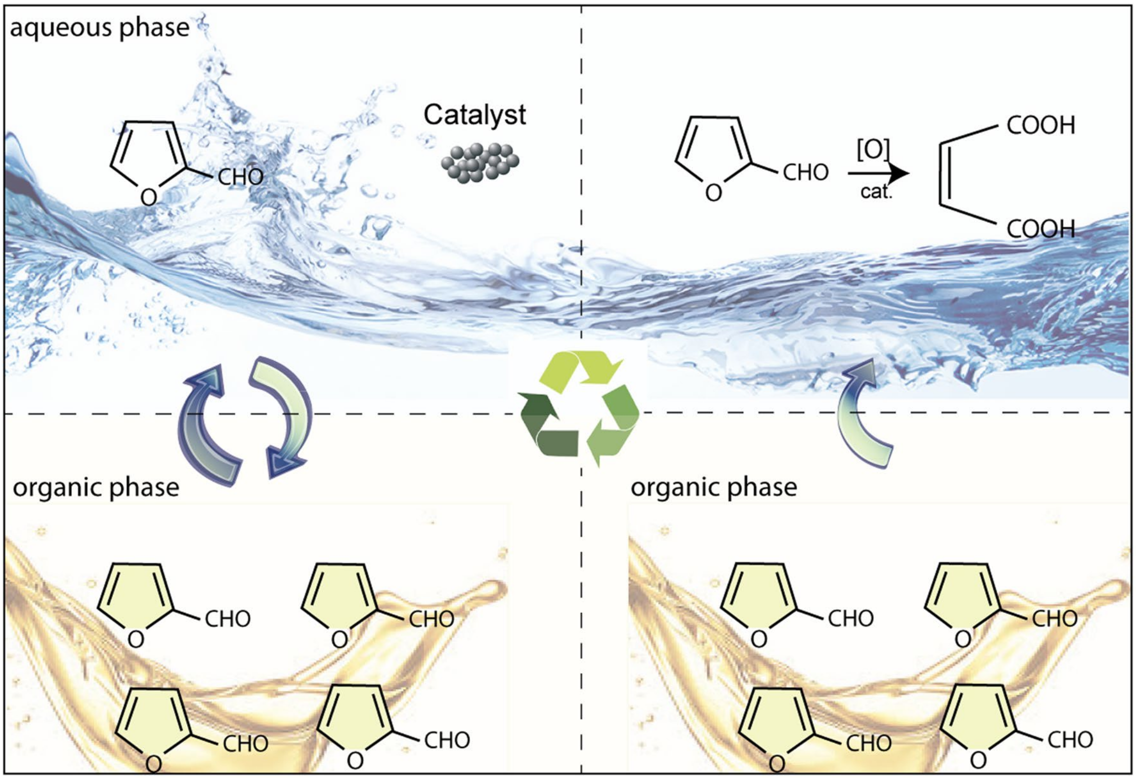


Figure 1 Simplified flow line of catalytic oxidation of furfural in biphasic system adapted from [31].

were observed over other metal catalysts. However, the major competitive process for the selective oxidation is the polymerization of furfural to generate resins under the oxidative conditions. The authors observed that in some experiments in the absence of a catalyst, the conversion of furfural was 56.3% with only a 7.2% yield of maleic acid. These results were explained by the polymerization of furfural to resins.

Table 1 shows the recent catalytic results obtained with different catalysts in liquid phase oxidation. The best results were obtained with heteropolyacids such as $H_3PMo_{12}O_{40}$, $H_3PMo_{12}O_{40}$ modified with $Cu(NO_3)_2$ and $VO(acac)_2$ (up to 52% of MA yield and 56% of selectivity to MA). This showed the influence of acidity of the catalysts on the overall catalytic activity in this reaction.

Some authors studied also the influence of the nature of counter-ions of the copper (II) cation, which could modulate the redox properties of the Cu^{2+} [26]. It was found that the acetate, sulfate and nitrate counterparts could significantly improve the yield of maleic acid. In contrast, using the chloride anion did not yield any improvement, and using carbonate even led to a detrimental effect on catalytic activity [32]. However, the extra addition of nitrate to the reaction mixture did not improve the catalytic activity at all, which suggests that the nitrate anion does not independently promote the conversion of furfural to maleic acid. However, it may play the role of modulator of the redox potential of Cu^{2+} to increase the catalytic oxidation efficiency [32].

Very interesting results were observed in the case of the combination of copper nitrate with phosphomolybdic acid. The mixture of these two reagents yielded a drastic enhancement of the reaction of furfural oxidation to maleic acid. For a mixture of 0.8 mmol of phosphomolybdic acid and 0.4 mmol of copper nitrate, the yield of maleic acid could be improved up to 49.2% with a selectivity of 51.7%, and the conversion of furfural was 95.2% (as compared to the test without $Cu(NO_3)_2$: 38.4, 43.3 and 88.7%, respectively) [32].

Muzyczenko et al. have studied the oxidation of furfural with hydrogen peroxide in water and in absolute ether containing small amounts of water [34]. They found

Table 1 Summary of catalytic results obtained in liquid phase

Catalyst	Conditions	Furfural or HMF conversion	MA yield	MA selectivity	References
$H_3PMo_{12}O_{40}$	383 K, O_2 20 bar, H_2O + nitrobenzene	67 (furfural)	38	56	[30]
$H_3PMo_{12}O_{40}$	383 K, O_2 20 bar, H_2O + toluene	73 (furfural)	37	50	[30]
$H_3PMo_{12}O_{40}$	383 K, O_2 20 bar, H_2O + *p*-xylene	66 (furfural)	35	53	[30]
$H_3PMo_{12}O_{40}$	383 K, O_2 20 bar, H_2O + cyclohexane	85 (furfural)	38	45	[30]
$H_3PMo_{12}O_{40}$	383 K, O_2 20 bar, H_2O + tetradecane	82 (furfural)	38	46	[30]
$H_3PMo_{12}O_{40}$	383 K, O_2 20 bar, H_2O	86 (Furfural)	38	44	[30]
$VO(acac)^2$	363 K, O_2 10 bar, CH_3CN	99 (HMF)	52	52	[31]
Amberlyst 15	353 K, H_2O_2, H_2O, 24 h	99 (furfural)	11	11	[33]
Nafion NR50	353 K, H_2O_2, H_2O, 24 h	99 (Furfural)	11	11	[33]
Nb_2O_5	353 K, H_2O_2, H_2O, 24 h	99 (furfural)	4	5	[33]
ZrO_2	353 K, H_2O_2, H_2O, 24 h	99 (furfural)	5	5	[33]
$H_6PV_3MO_9O_{40}$	383 K, O_2 20 bar, CH_3CN	99 (furfural)	12	12	[44]
$VO(acac)^2$	363 K, O_2 10 bar, DMF	96 (HMF)	7	7	[31]
$H_5PV_2Mo_{10}O_{40}$ + $Pd(OAc)_2$ (1/1)	383 K, O_2 20 bar, CH_3CN	94 (furfural)	14	15	[44]
$VO(acac)^2$	363 K, O_2 10 bar, TFT	96 (HMF)	7	7	[31]
$VO(acac)^2$	363 K, O_2 10 bar, CH_2Cl_2	99 (HMF)	16	16	[31]
$VOSO_4$	363 K, O_2 10 bar, CH_3CN	NC (furfural)	34	NC	[31]
$Co(OAc)_2$	363 K, O_2 10 bar, CH_3CN	NC (furfural)	2	NC	[31]
$Co(NO_3)_2$	371 K, O_2 20 bar, H_2O	69 (furfural)	4	6	[32]
$FeSO_4$	371 K, O_2 20 bar, H_2O	90 (furfural)	12	13	[32]
V_2O_5	371 K, O_2 20 bar, H_2O	72 (Furfural)	6	8	[32]
$CuSO_4$	371 K, O_2 20 bar, H_2O	67 (furfural)	19	29	[32]
$Cu(NO_3)_2$	371 K, O_2 20 bar, H_2O	86 (furfural)	24	28	[32]
$Cu(OAc)_2$	371 K, O_2 20 bar, H_2O	71 (furfural)	19	26	[32]
$H_3PMo_{12}O_{40}$ + $Cu(NO_3)_2$ (2/1)	371 K, O_2 20 bar, H_2O	95 (furfural)	49	52	[32]

NC Not communicated.

that the presence of water inhibits the formation of furfuryl hydroxyhydroperoxide but promotes the formation of acids. Moreover, the acids formed during the reaction catalyzed the other reaction steps. In the case of an excess of water, water molecules blocked the carbonyl group of furfural. The formation of hydrogen bonds with the carbonyl group and water prevails forming the furfural–H_2O complex, which hinders the access of H_2O_2 molecules to the furfural. In the case of the absence of water molecules, the formation of a polar furfural–H_2O_2 complex prevails [34].

Recently, Fagundez et al. studied the selective liquid-phase oxidation of furfural to maleic acid using hydrogen peroxide as an oxidant and titanium silicalite (TS-1) as a catalyst [35]. The highest yield of 78 mol.%, was obtained using an H_2O_2/furfural molar ratio of 7.5 at 323 K after 24 h of reaction (furfural/catalyst ratio of 1). However, Ti leaching was observed, especially during the first run, and became much less important in the subsequent successive cycles. In addition, the leaching affected both anatase and Ti species within a silicalite framework. Moreover, the authors observed that, when using pure furfural, the catalyst could be reused for five runs without noticeable deactivation, whereas when using furfural directly derived from biomass, visible deactivation occurred. It was explained by the presence of some organic impurities in biomass-derived furfural.

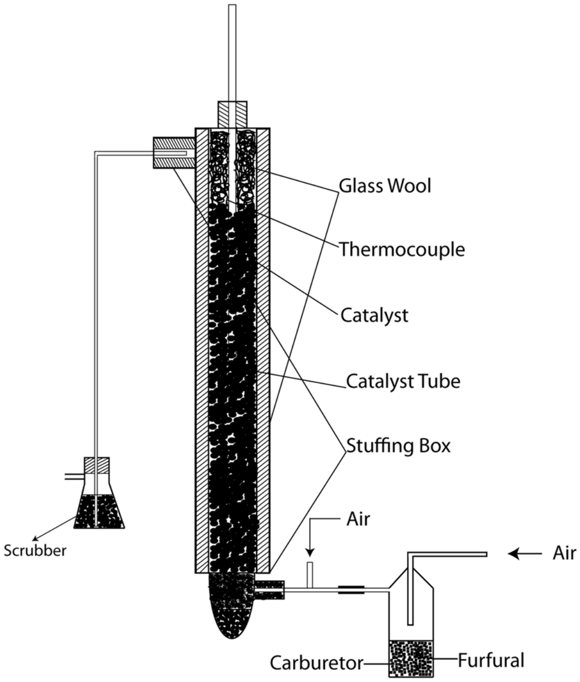


Figure 2 Nickel-tube reactor apparatus for gas phase furfural oxidation (reproduced with permission from American Chemical Society, Ref. [36]).

Gas phase oxidation: heterogeneous catalysis

Gas phase oxidation reactions are one of the most important processes in the chemical industry. The first catalytic tests to transform furfural into maleic acid were performed in the first half of the 20th century. In 1949, Nielsen reported on gas phase furfural oxidation to maleic acid based on iron molybdates materials and carried out in nickel-tube reactors as shown in Figure 2 [36].

In this study, three different materials were used as a reactor tube: nickel, iron and aluminum. It was shown that nickel enabled obtaining higher conversion rates as compared to Fe or Al tubes. The authors did not explain this phenomenon but assumed that nickel should be a good catalyst for one of the steps in furfural oxidation. The authors compared also two types of iron catalysts: iron molybdate impregnated on alumina and catalysts prepared by mixing iron nitrate and ammonium molybdate. The best catalytic results were obtained for the former, indicating the influence of method of preparation on catalytic activity (acidity of the catalyst). The authors claimed 95% or higher furfural conversion and over 80% of MA yield. These results were much better that those reported earlier in the literature [36–39].

Recently, Ojeda et al. reported that furfural could be converted into maleic anhydride (73% yield) through selective gas phase oxidation at 593 K with O_2 over VO_x/Al_2O_3 catalysts [40]. They were the first to undertake detailed investigations on the effects of VO_x structures on maleic anhydride formation by furfural oxidation. They found that at low surface VO_x densities (<2.5 at $V{\cdot}nm^{-2}$), highly dispersed vanadia species (monovanadates, VO_4) with one short $V=O$ terminal bond and three anchoring V–O–Al bonds are formed. With increasing vanadium surface density (>2.5 at $V{\cdot}nm^{-2}$), polyvanadates (V–O–V bonds) are expected to form gradually on the catalyst surface. The presence of various active species should then be related to different catalytic activities. Indeed, polyvanadates exhibited the highest normalized rate as compared to monovanadates and V_2O_5, which showed similar activities. Moreover, they found that increasing O_2 pressure exhibited a positive effect on furfural conversion. However, higher concentrations of O_2 led to less selective furfural oxidation and formation of furan (up to 9%).

Wang et al. [41] have studied V_2O_5–MoO_3–P_2O_5/γ–Al_2O_3 catalysts prepared by impregnation in the oxidation of furfural to maleic anhydride. The catalytic behavior of the catalysts was evaluated in a continuous fixed-bed reactor, using a feeding stream comprising 2% furfural in air at 578 K. The authors found that the activity depends on the MoO_3/V_2O_5 ratio. When this ratio was equal 0.4, the conversion of furfural reached 82% and the yield of maleic anhydride was close to 50%. The authors indicated that the introduction of MoO_3 adjusts the interaction between the support and the active phase. This enables the rapid exchange of crystal lattice oxygen in the catalysts and then accelerates the overall activity and improves the selectivity to maleic anhydride [41].

Shimanskaya et al. studied vapor-phase oxidation of furan to maleic anhydride in the presence of metal-containing catalysts [42]. High yields of maleic anhydride could be obtained. However, oxidation by-products such as carbon monoxide and dioxide with small amounts of acetic and oxalic acids were also observed. It was established that the vapor-phase oxidation of furan, in contrast to its derivatives, is more selective. The yield of maleic anhydride is higher, and complete transformation of the furan is achieved in a shorter period.

Mechanism of maleic acid formation

The maleic acid formation mechanism involves the removal of one or two carbon atoms from the considered starting reactant (furfural or HMF, respectively). Meanwhile, there is still no consensus on the role of the nature of the active phase and on the mechanism of the reaction. It has been claimed that MA can form via different pathways depending on the starting molecule (furan, furfural or HMF), which seems a reasonable assumption.

The oxidation of furan in the presence of vanadium (V) oxide takes place through a route involving the formation of an endoperoxide, [43] which is then oxidized to maleic anhydride, as described below (Scheme 3).

In the case of the furan molecule, the formation of maleic acid goes through a first step of ring opening before a subsequent step of oxidation of the aldehyde groups to acid groups.

In the oxidation of furfural to maleic acid, one atom of carbon must be removed. There are two potential pathways to lose one carbon atom through decarboxylation. The first consists on decarboxylation and then furan ring-opening while the second one starts with ring-opening and then proceeds through decarboxylation. Guo and Yin studied furfural oxidation mechanism on phosphomolybdic acid catalysts. They observed that neither furoic acid nor furan were the intermediates in the MA formation reaction. These results confirmed a two-step mechanism with furan ring opening as a first step and decarboxylation to MA as the final step. Moreover, they proposed a plausible mechanism based on a radical pathway as shown in Scheme 4.

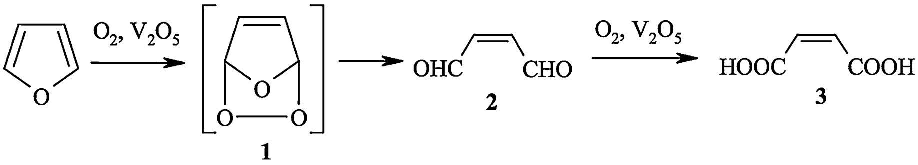
In this mechanism, the first hydrogen atom is abstracted by the oxygen or catalyst and results in the furfural radical formation. This radical can be transformed to furfural cation (via electron transfer to the catalyst) and further react with water to generate an intermediate compound easily oxidized to maleic acid [30].

A different mechanism of maleic acid formation from furfural in the gas phase was proposed by the Ojeda's group [40] (Scheme 5).

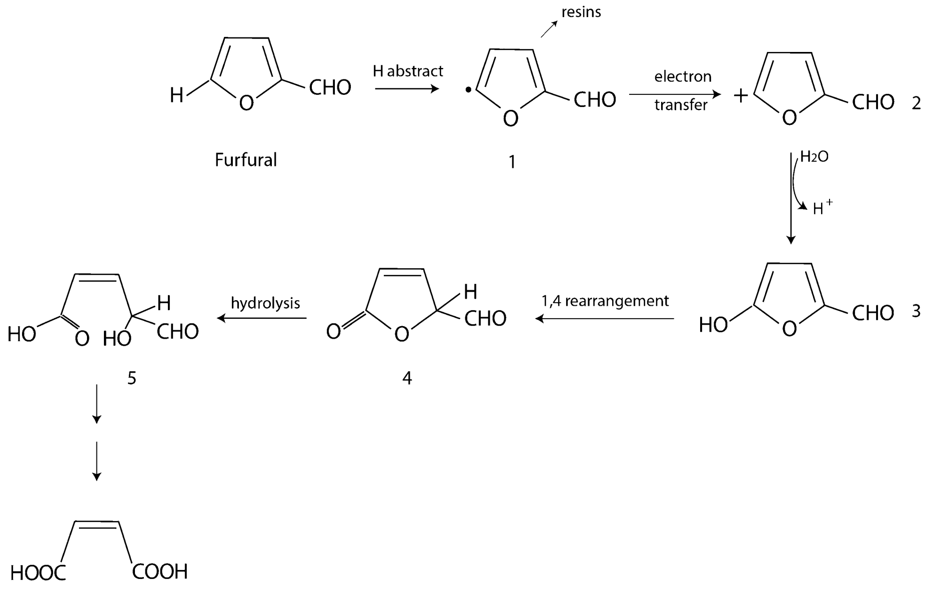
As described by these authors, first, furfural decarbonylation yields furan, which is the main reaction intermediate (Scheme 5). Subsequently, furan is oxidized in two steps, first to 2-furanone and then to maleic anhydride. CO_2 and H_2O could be formed through total oxidation of furfural and/or intermediate compounds. The authors carried out also kinetic studies of furfural oxidation. They found that neither furfural nor O_2 saturates the catalytic surface under the studied reaction conditions. Moreover, taking into account that furfural oxidation to maleic anhydride differs from zero-order kinetics towards O_2, it implies a different reaction pathway compared to the Mars–van-Krevelen mechanism. The authors then proposed a Langmuir–Hinshelwood model for the furfural oxidation over VO_x/Al_2O_3.

Lan et al. [44] proposed that the formation of maleic anhydride could be initiated from the furfural radical intermediate formed after the first hydrogen abstraction by oxygen. This radical can then attack the C = O bond of another furfural molecule to start polymerization or it can also initiate the formation of maleic anhydride as shown in Scheme 6.

In the most plausible pathway, the furfural radical generates the furfural cation intermediate, which is then attacked by a H_2O molecule to form the intermediate 4-hydroxyfurfural. This intermediate follows then a 1,4-rearrangement and decarbonylation to finally form maleic anhydride (Scheme 6). Moreover, as expected, the mechanism of maleic anhydride formation in the liquid phase is different from that observed in gas phase

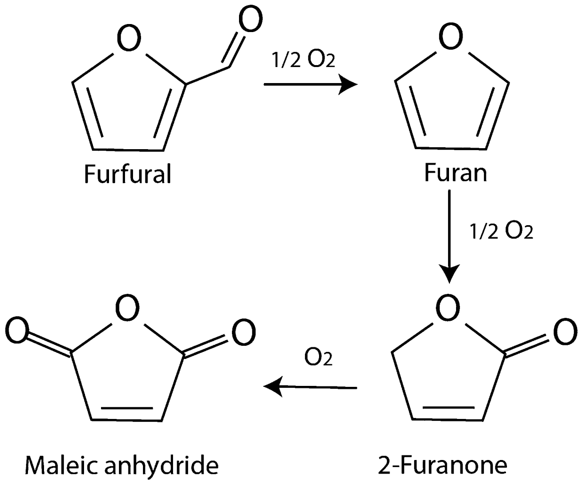


Scheme 3 Oxidation of furan and its homologs with molecular oxygen (reproduced with permission from Springer Science + Business Media, Ref. [43]).

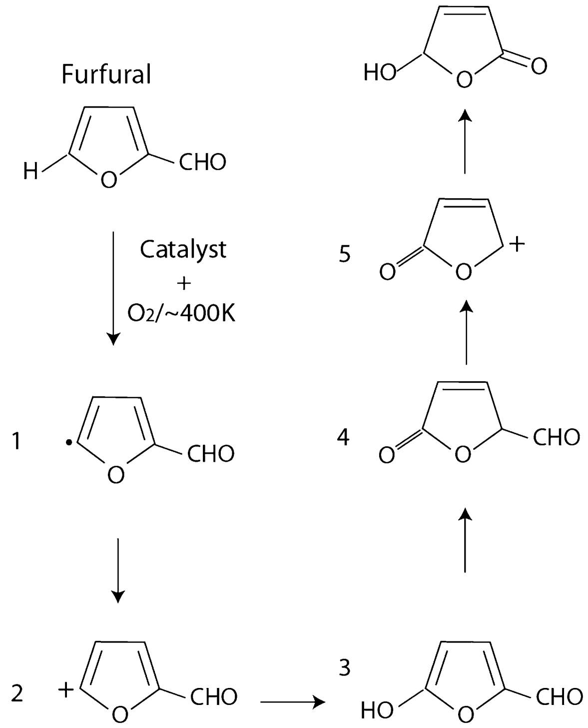


Maleic acid

Scheme 4 Catalytic oxidation of furfural on phosphomolybdic acid catalyst. Adapted from [30].



Scheme 5 Reaction pathways proposed for the selective oxidation of furfural to furan and maleic anhydride over VOx/Al_2O_3 catalysts [40].



Scheme 6 Plausible pathway of furfural oxidation to maleic anhydride [44].

oxidation of furfural. The same authors claimed that furan is not the intermediate in the maleic anhydride formation over the $H_5PV_2Mo_{10}O_{40}$ catalyst in the liquid phase [44].

The formation of CO_2 in vapor phase oxidation of furfural to maleic anhydride could originate from both direct oxidation of furfural or successive oxidation of maleic anhydride. Murthy compared three possible reactions schemes over vanadium pentoxide catalysts: parallel consecutive mechanism (parallel formation of CO_2 from furfural and maleic anhydride), parallel reaction (CO_2 originating from maleic anhydride is negligible) and consecutive mechanism (CO_2 formation from furfural is negligible). He found that the oxidation of furfural at 493-553 K followed the parallel reaction scheme. The experimental data were satisfactorily explained by the well-known two-stage redox mechanism of Mars and van Krevelen. The re-oxidation of the catalyst was found to be the rate-determining step in the investigated temperature range. Moreover, the order of the reaction was found to be one with respect to furfural and oxygen partial pressures [45].

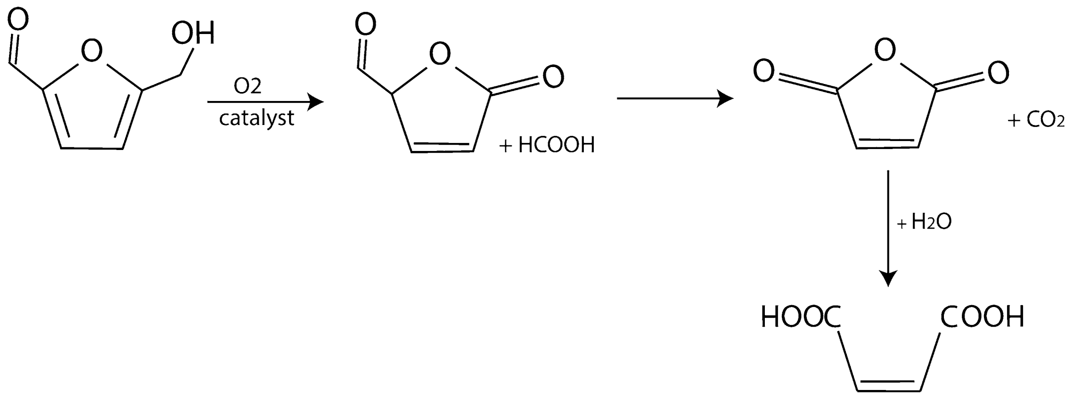
The formation of maleic acid from HMF involves a C–C bond cleavage and the removal of two carbon atoms. The mechanism of this reaction was studied by Du et al. [31] (Scheme 7). They showed that the aldehyde group of HMF was relatively stable under oxygen atmosphere, and that MA was probably not formed via a decarboxylation reaction. Indeed, intermediate compounds such as DFF or FDCA were not involved in the reaction mechanism. Moreover, they claimed that the formation of MA from HMF was related to the hydroxymethyl group of HMF rather than the aldehyde group, which was not necessary for C–C bond cleavage.

Choudhary et al. [33, 46] have studied oxidation of furfural with H_2O_2 to succinic acid (SA) on acid catalysts. High conversions of furfural and good selectivity to succinic acid were reported (74%). However, in some cases, relatively good selectivity to MA was also observed (up to 16% in the case of Amberlyst-15 catalyst). It was shown that the acid catalyst enhanced the efficiency of H_2O_2. FA was formed in higher yields than SA in the initial stages of the reaction. Thereafter, a decrease in the FA yield concomitantly with an increase in the MA yield was observed. This trend was explained by the low solubility of FA in water, which then converts to a highly soluble MA via isomerization. Interestingly, it is worth noting that such isomerization was enhanced by the formed formic acid in the presence of Amberlyst-15. The authors proposed two reaction pathways involving the Baeyer–Villiger oxidation. In the first step, the furan ring was opened up to undergo oxidation by H_2O_2. The pathway was well supported by experiments and revealed that MA is obtained from furan-*2*(*5*H)-one intermediate (Scheme 8).

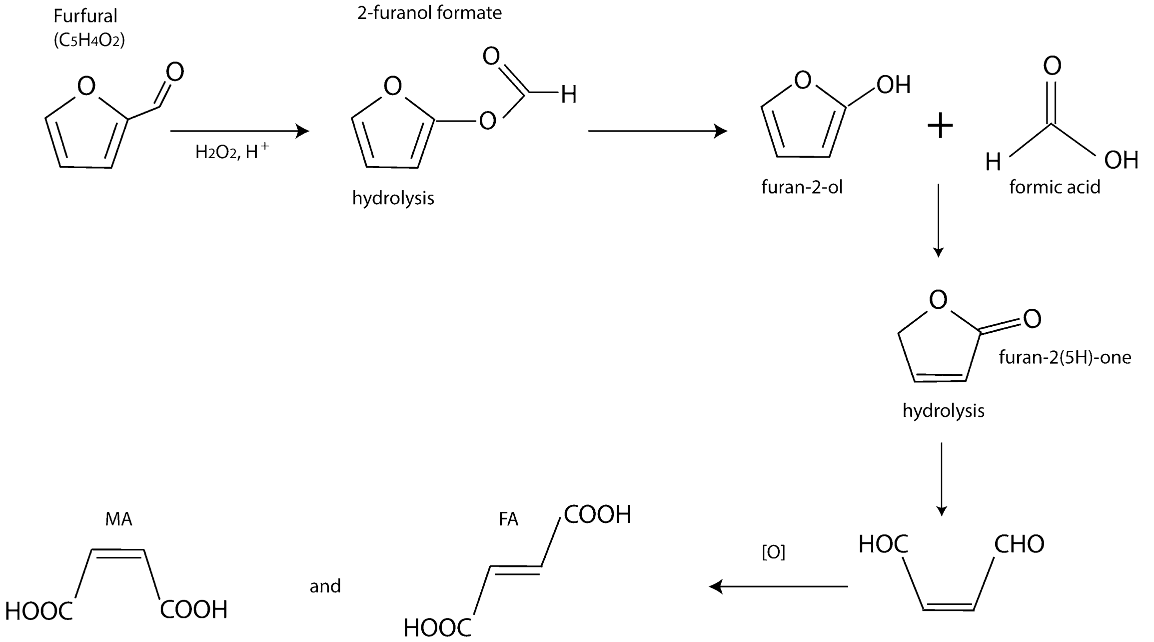
Conclusion

In this paper, we provide a close look at the existing literature on the preparation of maleic acid from biomass-based feedstocks via oxidation of HMF, furfural and furan. The oxidation can be carried out in gas or liquid phase. We report the best ways to obtain MA, MAnh or FA using O_2 or H_2O_2 as oxidants over widely available catalysts. The best results in term of MA selectivity were obtained in liquid phase using homogeneous $H_3PMo_{12}O_{40}$ and $VO(acac)_2$ catalysts. In the case of heterogeneous catalysis, the best results reported so far are obtained by vapor phase oxidation using vanadium oxide or vanadium-molybdenum mixed oxides supported on Al_2O_3. The liquid phase oxidation using heterogeneous catalysts still need improvement. Especially, the leaching of active phase should be avoided.

In this review, we put emphasis on the different mechanisms reported in the literature because fundamental studies are now essential in the design of the catalysts and optimization of conditions of the synthesis of these valuable chemicals. However, there is still no consensus on the exact mechanism of the reaction and the role of the nature of the active phase. It has been claimed in the literature that MA can form from furfural via different pathways: (1) abstraction of hydrogen to form furfural radical intermediate that then gives 4-hydroxyfurfural; (2) decarboxylation of furfural to furan, which then gives a 2-furanone intermediate; or by (3) first Baeyer–Villiger oxidation of furfural to furan-2-ol and then to MA through furan-*2*(*5*H)-one intermediate. The next challenge in the synthesis of maleic acid will be the elaboration and the use of efficient heterogeneous catalytic



Scheme 7 Possible mechanism of *5*-hydroxymethylfurfural (HMF) oxidation with O_2 in liquid phase. Adapted from [31].



Scheme 8 Mechanism of furfural oxidation with H_2O_2 via Baeyer–Villiger oxidation. Adapted from [33, 46].

systems working under «green conditions», i.e., using low temperature and environmentally friendly solvents.

Abbreviations

MA: maleic acid; MAnh: maleic anhydride; FA: fumaric acid; HMF: 5-hydroxymethyl furfural; SA: succinic acid; VPO: vanadium — phosphorus — oxide; FAlc: furfuryl alcohol; THFA: tetrahydrofurfuryl alcohol; DFF: 2,5-diformylfuran; DMF: N,N-dimethyl-formamide; TFT: α,α,α-trifluorotoluene; acac: acetylacetone; OAc: acetoxy group; TS-1: titanium silicate; FDCA: 2,5-furandicarboxylic acid.

Authors' contributions

RW, FS, SP, FD, FC, RVG have been involved in drafting of this manuscript and in revising it critically for important intellectual content. All authors read and approved the final manuscript.

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Compliance with ethical guidelines

Competing interests

The authors declare that they have no competing interests.

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