INCOMPLETE CATALYTIC OXIDATION OF FURAN COMPOUNDS (REVIEW)

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The catalytic oxidation of furan compounds in the vapor and liquid phases is reviewed.

The vapor-phase and liquid-phase oxidation of furan compounds is a catalytic method for the synthesis of maleic anhydride, lactones, and furancarboxylic acids and their derivatives. The greatest number of studies in the area of the liquid-phase oxidation of furan compounds have been devoted to the oxidation of furfural and other furan compounds with molecular oxygen (autooxidation) and hydrogen peroxide.

The mechanism of these reactions has been discussed in detail in review papers [1, 2] and dissertations [3, 4].

The subject of the present review is the vapor-phase oxidation of furan compounds on vanadium catalysts and their liquid-phase oxidation on heterogeneous oxide (Ag_2O, Ag_2O-CuO, etc.) catalysts and in the presence of homogeneous catalysts (salts of metals with variable valences).

Vapor-Phase Oxidation of Furan Compounds on Vanadium Catalysts

Catalysts. The desired product in the vapor-phase oxidation of furan compounds on vanadium catalysts is maleic anhydride, which is a valuable monomer for the preparation of lacquers and glass plastics, defoliants and herbicides, dyes for polychromatic printing, nutritive acids, etc.

The catalysts for the vapor-phase oxidation of furan compounds can be divided into the following principal groups with respect to their activity and genesis.

1) Promoted V–Mo–P catalysts on aluminum metal prepared by the paste method [5, 6]. These catalysts are in a state that ensures high yields of maleic anhydride (70-80%) only when the reaction mixture is highly diluted with air. The efficiency of the catalysts does not exceed 1.5 g/liter · h.

2) Promoted V–Mo–P catalysts prepared by evaporation in an ammoniacal medium and applied to aluminum metal or nickel–aluminum alloy [7-12]. Under optimum conditions the desired product is obtained in 55-66% yield with an efficiency of up to 60 g/liter · h.

3) Promoted V–Mo–P catalysts on synthetic corundum, porcelain, carborundum, or other nonmetallic supports and prepared by evaporation in a hydrochloric acid medium [13]. Maleic anhydride is obtained in 47-63% yields at efficiencies of up to 130 g/liter · h.

Thus, depending on the composition and origin of the catalyst, the yield of the desired product changes by a factor of two and the catalyst efficiency changes by one order of magnitude. An increase in the initial concentration in the reaction mixture leads to a decrease in the selectivity of the process.

The best weight ratios of the active components in the case of oxidation of furfural on vanadium-containing catalysts applied to corundum and prepared by evaporation in a hydrochloric acid medium are as follows [13]: $MoO_3/V_2O_5 = 0.3\text{-}2.2$, $Ni/V_2O_5 = 0.006\text{-}0.03$, $P_2O_5/V_2O_5 = 0.005\text{-}0.02$, $Na/V_2O_5 = 0.005\text{-}0.02$, and $Na/P_2O_2 = 1$.

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Both a solid solution of molybdenum trioxide in vanadium pentoxide and a more complex catalytic system [14] characterized by a high MoO_3/V_2O_5 ratio (1-2.2) have high catalytic activity. A chemical compound is formed at these ratios of the catalytic oxides [15].

A characteristic peculiarity of the catalysts for oxidation of furan compounds is the presence of phosphates in the catalyst composition. Modification of the catalyst with monosodium phosphate (in $\sim 5\%$ concentrations) leads to the formation of a new chemical compound of the sodium phosphomolybdate type [16]. The bond between oxygen and the vanadium and molybdenum ions is broken, and the concentration of solitary V^{4+} ions changes. As in the case of vanadium–phosphorus catalysts for the oxidation of C_4 hydrocarbons [17, 18], the role of phosphorus compounds in multicomponent vanadium catalysts reduces to weakening of the $V{=}O$ bond of the vanadium pentoxide.

Oxides of silver, thallium, cadmium, cobalt, lanthanum, cerium, etc., which can be arranged in the order $Ag_2O \geq Tl_2O_3 > CdO \geq NiO > CeO_2$ with respect to the effect of an increase in selectivity, have been proposed [19, 20] as promoters for V–Mo–P catalysts.

The increase in selectivity observed when promoting compounds are introduced in the catalyst composition is due to the change in the ratio of the rates of the partial reactions involving the formation of maleic anhydride and complete oxidation of the furan compound. Rearrangement of the structures of the catalysts is observed when various additives are introduced [16, 21, 22]. Modification of the catalyst with added Ag_2O leads to the formation of silver–vanadium bronze AgV_6O_{15}, silver polyvanadate AgV_7O_{18}, and unbonded AgCl [23]. Cupric oxide-promoted catalysts contain a copper–vanadium bronze [16]. Silver polyvanadate and silver- and copper–vanadium bronzes contain vanadium ions surrounded by oxygen with various bond energies; the high heterogeneity of the surface with respect to oxygen ensures high selectivity of these catalysts during incomplete oxidation of furan compounds and hydrocarbons [23, 24].

Modification of catalysts by the addition of CeO_2 and In_2O_3 leads to a change in the bond between the vanadium ion and oxygen because of the transition of a portion of the vanadium ions to octahedral coordination [16]. These catalysts are characterized by relatively low selectivity as compared with silver-promoted catalysts.

Synthetic corundum, carborundum, mullite, chamotte, TiO_2, nickel–aluminum alloys, and other forms of supports can be used as supports for catalysts for the vapor-phase oxidation of furan compounds. The selectivity of a catalyst increases as the porosity of the support decreases [25]. The optimum supports are those characterized by an overall porosity $\leq 7\%$. When the porosity is increased to 47%, one observes a sharp decrease in the selectivity of the oxidation of furan compounds as a result of transition of the reaction to the intradiffusion region.

At comparable support porosities, the distribution of the pores along the radius has a great effect on the properties of the catalyst. The optimum supports are those characterized by the presence of large transport pores ($r \geq 1000$ Å) and a minimum percentage of fine pores with radii < 100 Å. Prior treatment of nonmetallic supports with concentrated HCl has been recommended [26]. The role of the latter consists in dissolving and removing iron salts and increasing the percentage of large transport pores.

The conditions under which the catalyst is generated have a considerable effect on the particle size and structure of vanadium catalysts. The best method for the preparation of the catalysts is evaporation of a solution of the active components in the presence of the support [27, 28]. It has been established by comparison of the structure and particle size of vanadium catalysts prepared by evaporation in hydrochloric acid and ammoniacal media that the catalysts prepared in hydrochloric acid media are characterized by a more finely dispersed system of catalytic oxides. The differences in the degree of dispersion of the layer of active components are responsible for the different mechanical strengths of the above catalysts. The degree of dispersion of the catalytic oxides for catalysts prepared in hydrochloric acid media is one order of magnitude lower than that of catalysts prepared in ammoniacal media [14]. This difference in the structure and properties of catalysts prepared in hydrochloric acid and ammoniacal media is associated with the fact that crystalline V_2O_5 is formed by dehydration of $V_2O_5 \cdot nH_2O$ during activation of compounds obtained from acid solutions, while crystallization of V_2O_5 from vanadium compounds obtained from ammoniacal solutions occurs during thermal decomposition of NH_4VO_3.

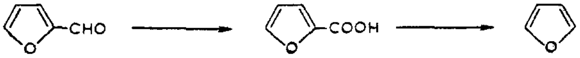
The technology for the production of pilot-plant batches of promoted vanadium–molybdenum–phosphorus catalysts on corundum or aluminum metal has been worked out. The vanadium–molybdenum–phosphorus catalyst on corundum is characterized by high reproducibility of the catalytic activity during the production of large batches. This catalyst has proved its value in the case of its utilization for 2 yr in a pilot-plant installation with an output of 250 tons/yr both with respect to the activity of the catalyst and the quality of the desired product. The technology for the isolation of maleic anhydride from the contact gases has been worked out [16, 29].

Thus a new and original method for the production of maleic anhydride for the paint and varnish industry from a material that has not been previously used for this process – furfural – has been created. The vapor-phase oxidation of furfural is a promising method for the preparation of maleic anhydride in countries that have large sources of pentosan-containing raw material and limited petroleum reserves.

The preparation of maleic anhydride by the vapor-phase oxidation of furan – a side product in the oxidative dehydrogenation of butenes and butadiene – is a promising method [30, 31]. The vapor-phase oxidation of furan to maleic anhydride is characterized by a high yield of the desired product and high efficiency of the process (~80 mole % and 240 g/liter · h) [32].

Reactivities of Furan Compounds and the Reaction Mechanism. The reactivities of furan compounds have been studied under integral [33] and nongradient [34, 35] conditions. The rate of accumulation of maleic anhydride and the rate of the overall conversion of furan compounds decrease in the order [34] furan > furfural > tetrahydrofuran (THF) > furfuryl alcohol > α-methylfuran > 5-methylfurfural.

The first and slow step in the oxidation of furan derivatives to maleic anhydride is oxidative elimination of the side chain. The latter is in agreement with the hypothesis of M. V. Shimanskaya and S. A. Giller [36] and Milas and Walsh [33]. Furan has been proposed as the intermediate in the formation of maleic anhydride from furfural:



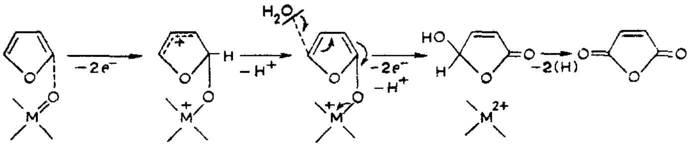
Evidence in favor of this assumption is provided by the data in [37], according to which oxidative decarbonylation of furfural to furan occurs on vanadium catalysts in the presence of oxygen and water.

Data on the liquid-phase oxidation of α-^{14}C-furfural constitute a second piece of evidence in favor of the above mechanism. The maleic and fumaric acids formed do not contain radioactive carbon [38]. A comparison of the energy of cleavage of the C–H bond of the furan ring and the C–H bond of the carbonyl group indicates primary oxidation of the aldehyde group.

With allowance for the quantum-chemical reactivity indexes of the individual structural elements of the furan molecule, it has been assumed that reaction in the 2 and 5 positions of the furan ring occurs in the case of oxidation of furan to maleic anhydride, whereas reaction of the surface forms of furan and oxygen in the 2 and 3 positions of the furan ring occurs in the case of complete oxidation [39].

The singly charged (in the 2 position) furyl cation and the doubly charged (in the 2 and 5 positions) dication are probably intermediate forms in the production of maleic anhydride [40]. In analogy with the oxidation of other organic compounds [41-43], it has been proposed that the oxygen anion radicals O^-, O_2^-, and $O_2^- \cdot O_2$ and loosely adsorbed oxygen participate in the oxidation of furan compounds. It has been assumed that the oxidation of furan to maleic anhydride proceeds either with opening of the furan ring through a step involving the formation of maleic dialdehyde [33] or with retention of the furan ring through a step involving the formation of the hypothetical 2,5-dihydroxyfuran [8].

Veiss and co-workers [44] explain the oxidation of furan to maleic anhydride on vanadium catalysts with allowance for the electrophilic reaction of the catalyst with the carbon atoms of the furan ring in the 2 position:



Vanadium oxide catalysts are capable of this sort of reaction owing to the pronounced electrophilic character of their oxidative groups. The mechansm of the formation of maleic anhydride includes several steps – electrophilic attack, deprotonation, and reaction of the corresponding carbonium ion with a hydrogen donor (water) to give the corresponding hydroxy ketone as an intermediate. An advantage of this hypothesis as compared with the previous hypotheses is the assumption of the participation of the V=O group of the catalyst in the oxidative process. A number of researchers have established a correlation between the presence of

TABLE 1. Kinetic Principles of the Oxidation of Furan Compounds on an Ni- and Na-Promoted V–Mo–P Catalyst on a Carborundum Support (s_{sp} = 0.82 m^2/g)*

Compound undergoing oxidation	Exptl. conditions	Form of the kinetic equations	E_a, kcal/mole	Effective activation entropy, eu
Furan	290—350°; $v=11600—97000\ h^{-1}$, $c_0=1{,}4\cdot10^{-4}$— $3{,}7\cdot10^{-4}$ mole/liter $[O_2]=5\cdot10^{-3}$— $44\cdot10^{-3}$ mole/liter	$w_{tot}=k_{tot}[O_2]$ $w_{MA}=k_{MA}[O_2]$ $w_{CO}=k_{CO}[O_2]^{0,7}$ $w_{CO_2}=$ $=k_{CO_2}c^{0,8}[O_2]^{0,6}$ $w_1=k_1[O_2]$ $w_2=k_2c^{0,4}[O_2]$	$E_{tot}=33$ $E_{MA}=41$ $E_{CO}=29$ $E_{CO_2}=27$ $E_1=41$ $E_2=28$	$S^*{}_{1eff}=-2{,}6$ $S^*{}_{2eff}=-4{,}0$
Furfural	302—350°; $v=8000—36000\ h^{-1}$ $c_0=1{,}7\cdot10^{-4}$— $3{,}4\cdot10^{-4}$ mole/liter $[O_2]=5{,}5\cdot10^{-4}$— $4\cdot10^{-2}$ mole/liter	$w_{tot}=$ $=k_{tot}c^{0,4}[O_2]^{0,5}$ $w_{MA}=$ $=k_{MA}c^{0,8}[O_2]^{0,8}$ $w_1=k_1c^{0,5}[O_2]^{0,7}$ $w_2=k_2$	$E_{tot}=26$ $E_{CO_2}=30$ $E_{MA}=35$ $E_1=34$ $E_{CO}=23$ $E_2=21$	$S^*_{eff_{tot}}=$ $=-24{,}6$ $S^*_{eff_{MA}}=$ $=-5{,}7$
5-Methylfurfural	302—370°; $v=2000—32700\ h^{-1}$ $c_0=1{,}7\cdot10^{-4}$— $3{,}7\cdot10^{-4}$ mole/liter $[O_2]=0{,}5\cdot10^{-2}$— $4{,}4\cdot10^{-2}$ mole/liter	$w_{tot}=$ $=k_{tot}c^{0,2}[O_2]^{0,6}$ $w_{MA}=k_{MA}[O_2]^{0,8}$ $w_1=k_1[O_2]^{0.8}$ $w_2=k_2c^{0,4}[O_2]^{0,3}$	$E_{tot}=25$ $E_{MA}=32$ $E_1=33$ $E_2=24$	$S^*_{eff_{tot}}=$ $=-30{,}4$ $S^*_{eff_{MA}}=$ $=-27{,}1$

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*Abbreviations: w is the rate (moles/$m^2\cdot h$), tot refers to total conversion of the furan compound, MA pertains to the maleic anhydride accumulated during the reaction, CO and CO_2 pertain to the formation of carbon monoxide and dioxide, and 1 and 2 pertain to the partial reactions of formation of maleic anhydride and complete oxidation of the raw material.

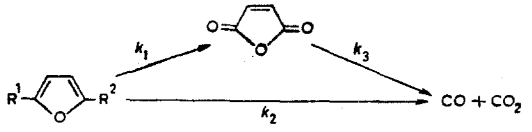
M=O in the catalyst and the selectivity of the process [18, 45]. The formation of one or the other intermediate depends, in addition to other conditions, on the orientation of the adsorbed furan on the catalyst surface. M. V. Shimanskaya and co-workers [16] have made a quantum-chemical calculation by the extended Hückel method (EHM) of the electron-density distribution in the positively charged furan ion and have estimated the magnitude of the transfer of electron density from the ligand to the crystal lattice in the case of a threefold orientation of the ligand above the vanadium ion. The maximum transfer of electron density takes place in the case of a plane-parallel orientation of the furan molecule above the vanadium ion, in which case the hydrogen atoms bonded to the C atoms in the 2 and 5 positions of the furan ring are closest to the oxygen atoms of the vanadium pentoxide lattice. A perpendicular orientation of the furan ring along the –C=C– bond on the catalyst surface has been proposed for the complete oxidation of furan compounds [39]. The above-mentioned forms of orientation of the furan molecule were established during a study of the adsorption of furan on the homogeneous surface of graphitized carbon black [46].

Kinetics of the Oxidation of Furan Compounds. We made the first studies of the kinetics of the oxidation of the most widespread compounds of the furan series (furan, furfural, and 5-methylfurfural) to maleic anhydride on promoted catalysts [47-52]. The reaction conditions, the forms of the kinetic equations, and the activation energies and effective activation entropies are presented in Table 1.

The oxidation of furan takes place in the region of high degrees of coverage of the surface with furan and low degrees of coverage with oxygen. The fractional orders with respect to the steady-state concentrations of the oxidizable component and oxygen during the oxidation of other furan compounds constitute evidence for the primary occurrence of these reactions in the region of medium degrees of surface coverage.

Competition between furfural and 5-methylfurfural for the active centers, which is expressed in terms of a considerable decrease in the rate of overall oxidation of furfural in the presence of 5-methylfurfural, has been established [20].

Products of complete oxidation are formed primarily in the case of direct oxidation of furan compounds (via a parallel scheme), and only a small portion of the complete-oxidation products (~15%) are formed via the consecutive total oxidation of maleic anhydride. The parallel-consecutive vapor-phase oxidation of furan compounds proceeds primarily in two parallel directions:



R^1 = H or CH_3 ; R^2 = H or CHO

In analogy with our studies, Novella and co-workers [53, 54] also propose a parallel-consecutive scheme for the process.

The existence of the reaction of furfural with maleic anhydride to give an adduct that is oxidized to carbon monoxide and dioxide under the reaction conditions has been assumed. However, this assumption contradicts the experimentally established absence of slowing down of the reaction rate by the reaction products.

First-order equations with respect to the surface concentration of furfural have been proposed for the description of the rates of the partial reactions [53, 54]. The reaction order with respect to oxygen has not been estimated.

The apparent activation energy (14.5 kcal/mole) for the formation of maleic anhydride is practically equal to the activation energy for the formation of maleic anhydride obtained by oxidation of furfural on a vanadium–molybdenum–phosphorus catalyst applied to aluminum metal.

In contrast to [53, 54], in our studies we established different orders of the partial reactions with respect to the oxidizable component. This also constitutes evidence for the formation of maleic anhydride and for complete oxidation of furan compounds via a parallel mechanism on different centers of the heterogeneous surface of the catalyst.

In the case of oxidation of furfural on two forms of vanadium–molybdenum–phosphorus catalyst it was established that the mechanism of the process does not change but the reaction takes place at a different degree of coverage of the surface with furfural. The rate of accumulation of maleic anhydride depends on the oxygen concentration to a greater degree than does the rate of complete oxidation, i.e., the selectivity of the reaction increases as the oxygen concentration increases [55, 56].

An increase in the selectivity as the temperature rises is also observed in the oxidation of furan compounds. The close apparent activation energies for the same reactions in the case of oxidation of a different form of raw material indicate identical orientations of the reacting particles on the catalyst surface. An analysis of the effective activation entropies provides evidence for relatively high lability of the transition state and for the similar nature of the activated complexes in the formation of maleic anhydride and the products of complete oxidation from furan. The ratios of the distribution functions of the activated complex and adsorbed furan (f^+/f_F) also indicate high lability of the activated complex in the formation of maleic anhydride from furan [39]. The latter indicates reoxidation of the vanadium catalyst as one of the slow steps in the oxidation of furan. Ideas regarding reoxidation of the catalyst as a slow step have also been expressed on the basis of kinetic data on the oxidation of furfural on vanadium catalysts [57].

The favorable influence of added water on the course of the process has been demonstrated in the case of oxidation of furan compounds [12, 58]. The selectivity of the formation of maleic anhydride increases and the amount of resins and volatile acids decreases in the presence of water. The favorable influence of water is due mainly to inhibition by water of homogeneous oxidation of furfural by molecular oxygen (autooxidation), particularly at low water concentrations in the reaction mixture. In addition, water participates in the adsorption displacement of furfural and maleic anhydride from the catalyst surface, thereby preventing their condensation with the reaction intermediates to give compounds that are difficult to desorb.

Furan compounds are arranged in the order furfuryl alcohol ≥ 5-methylfurfural > furfural > furan ≃ tetrahydrofuran with respect to the effect of increasing selectivity in the presence of water vapor.

In contrast to the positive effect of water vapor on the reaction, enrichment of the reaction mixture with a hydrogen donor (ammonia) leads to a sharp decrease in the selectivity of the process and an increase in the amount of resins in the reaction products [59]. The large role of volume parasitic processes in the conversion of furfural and other furan compounds in the presence of ammonia has also been established in the oxidative ammonolysis of furan compounds on vanadium catalysts [60-62]. The latter is due to the high reactivities of furan compounds in reactions involving condensation with ammonia.

In addition to the chief reaction products (maleic anhydride and carbon monoxide and dioxide), volatile and other acids, the qualitative and quantitative composition of which depends on the nature of the compound undergoing oxidation, are formed in the vapor-phase catalytic oxidation of furan compounds [63-75]. The overall rate of formation of the volatile acids depends on a fractional power (0.7) of the steady-state furfural concentration and is characterized by an apparent activation energy of 12 kcal/mole at 250-330° and 35 kcal/mole at 330-370°. The volatile acids and the resinous products are formed both in homogeneous processes involving autooxidation of furfural and in heterogeneous and heterogeneous-homogeneous processes involving condensation of furfural and its intermediate transformation products.

A characteristic peculiarity of the kinetics of the vapor-phase oxidation of furan compounds is a decrease in the rate as the initial concentration of oxidizable component in the reaction mixture increases [49].

The effect of water vapor, the peculiar kinetic principles in the formation of volatile acids, and the observed effect of slowing down of the reaction as the initial concentration of the oxidizable compound increases constitute evidence for a complex heterogeneous-homogeneous mechanism for oxidation of furan compounds. The heterogeneous oxidation of furan compounds to maleic anhydride is accompanied by their homogeneous oxidation by molecular oxygen (autooxidation), and this leads to the formation of resins and volatile acids.

The heterogeneous formation of maleic anhydride and complete-oxidation products is, in turn, accompanied by parasitic reactions involving the condensation of the intermediates with furfural on the catalyst surface. The existence of side reactions, as a result of which difficult-to-desorb substances are formed, has a pronounced effect on the kinetics of the principal heterogeneous catalysis process. Kinetic equations were derived from the steady-state conditions with allowance for slowing down of the reaction rate by the intermediates. The rate of overall conversion of furfural on a vanadium–molybdenum–phosphorus catalyst is expressed by the equation

$$\frac{dx}{d\tau}=\frac{k_1(1-x)\sqrt{\mathrm{O}_2}}{\mathrm{C}_0\left(1-x+b\frac{dx}{d\tau}\right)},$$

where k_1 and b are constants, C_0 and O_2 are the initial furfural and oxygen concentrations, x is the degree of conversion, and τ is the contact time.

Considering the high adsorption capacities of furan and other furan compounds, one must increase the oxygen concentration in the gas mixture to prevent the reaction of the transition complex with the starting compound to give difficult-to-desorb products. This is evidenced by the absence of a slowing-down effect in the oxidation of furan compounds with oxygen. Data on the adsorption of furan and oxygen on vanadium-containing catalysts [66], according to which furan is sorbed rapidly and completely irreversibly with 60% coverage of the surface by a monolayer, constitute evidence in favor of the proposed mechanism for the oxidation of furan compounds.

Thus the high adsorption capacities of furan compounds are due to a number of peculiarities of the kinetics of their oxidation as compared with the kinetic principles of the oxidation of aromatic compounds [67, 68]. These include the increase in selectivity as the temperature increases, the oxygen and water vapor concentrations in the reaction mixture, and the effect of slowing down of the reaction rate by the intermediates.

Liquid-Phase Oxidation of Furan Compounds

The greatest number of studies have been devoted to the liquid-phase oxidation of furfural to pyromucic acid on heterogeneous catalysts. These catalysts include oxide catalysts containing Mn, Al, Fe, Ni, Ag, and Au, as well as binary Ag–Cu oxide catalysts [69-77].

Liquid-phase oxidation of furfural has also been accomplished on Ag_2O–CuO catalysts applied to carbon and other supports [78, 79]. The use of applied catalysts facilitates their isolation from the oxidate and their regeneration.

According to [80], the liquid-phase oxidation of furfural on an Ag–Cu oxide catalyst proceeds via the following scheme:

$$\mathrm{Ag_2O+C_4H_3O-CHO+NaOH\rightarrow 2Ag+C_4H_3O-COONa+H_2O;}$$
$$\mathrm{2Ag+2CuO\rightarrow Ag_2O+Cu_2O;}$$
$$\mathrm{Cu_2O+1/2O_2\rightarrow 2CuO.}$$

The role of CuO in the composition of the binary Ag_2O–CuO catalyst reduces to oxidation of silver metal to silver oxide.

The oxidation is carried out in an alkaline medium to avoid decarboxylation of the pyromucic acid and other side reactions.

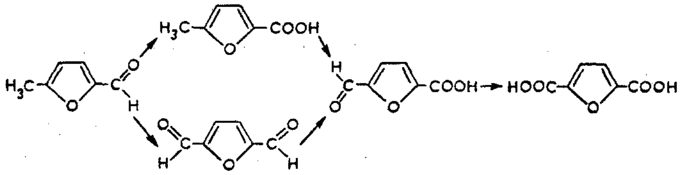
Liquid-phase oxidation of furfural with oxygen on a heterogeneous Ag—Cu oxide catalyst is characterized by high selectivity (91-95%) and the simplicity of the technology of the process. The catalytic synthesis of pyromucic acid therefore has advantages over the liquid-phase oxidation of furfural with potassium permanganate [76] and other synthetic methods.

The kinetics of the liquid-phase oxidation of furfural on an Ag—Cu oxide catalyst have been investigated [79, 81]. The rate is initially independent of the furfural concentration. At higher degrees of conversion the reaction rate is first-order with respect to furfural and the catalyst. Mass transfer between the gas—liquid and liquid—solid phases does not affect the rate of the process. The construction of a reactor for the liquid-phase oxidation of furfural has been proposed, and a mathematical model of the process has been worked out.

Heterogeneous Ag_2O and Ag_2O-CuO catalysts are also characterized by high activity in the oxidation of other compounds of the furan series.

We have shown that the liquid-phase oxidation of 5-methylfurfural with air oxygen in the presence of Ag_2O in an alkaline medium is a convenient method for the synthesis of 5-methylpyromucic acid [82]. However, the selectivity of the oxidation of 5-methylfurfural is considerably less than the selectivity of the oxidation of furfural. The yield of 5-methylpyromucic acid does not exceed 50 mole %.

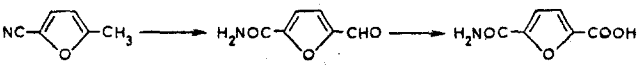
Whereas the principal product in the liquid-phase oxidation of 5-methylfurfural on a heterogeneous Ag_2O catalyst is 5-methylpyromucic acid, the chief product in the oxidation of 5-methylfurfural with air oxygen under pressure in the presence of a homogeneous catalyst — salts of metals with variable valences (a Co—Mn—Br catalyst) — is furan-2,5-dicarboxylic acid (in 36 mole % yield) [83]. The liquid-phase oxidation of 5-methylfurfural to furan-2,5-dicarboxylic acid proceeds via a parallel-consecutive scheme:



This process is accompanied by oxidative cleavage of the furan ring. This is responsible for the relatively low selectivity of the oxidation of 5-methylfurfural to oxygen-containing derivatives of the furan series as compared with the selectivity of the oxidation of alkylbenzenes [84].

The preparation of furan-2,5-dicarboxylic acid by the liquid-phase oxidation of 5-hydroxymethylfurfural with air oxygen on heterogeneous Pd—, Pt—, and Ag_2O-CuO catalysts is also known [85]. The process is relatively highly selective but is based on the use of a raw material that is difficult to obtain.

The liquid-phase oxidation of 5-methyl-2-cyanofuran with air oxygen in the presence of a cobalt—manganese catalyst under pressure in a solution of acetic acid has been studied [86]. Under these conditions, in addition to oxidation of the methyl group, one observes hydrolysis of the CN group to an amido group:



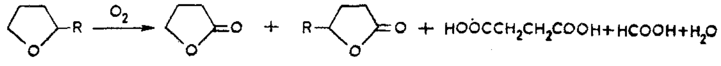
Depending on the reaction conditions, the process may be directed either to favor the predominant formation of furan-2,5-dicarboxylic acid monoamide or to favor the formation of 5-formylfuran-2-carboxamide.

A great deal of attention has been directed to the liquid-phase oxidation of THF and its derivatives [87-93]. Oxidation of THF with oxygen in the presence of peroxides or metals with variable valences or in the case of initiation by UV irradiation leads to the formation of α-hydroxytetrahydrofuran and γ-butyrolactone. The reaction proceeds via a chain mechanism to give the corresponding α-hydroperoxide as the primary molecular product. α-Hydroxytetrahydrofuran is an extremely reactive compound that exists in equilibrium with γ-hydroxybutyraldehyde. α-Hydroxytetrahydrofuran is converted to γ-butyrolactone at a high rate even under mild oxidation conditions and in the case of low degrees of conversion of the raw material.

We have investigated the liquid-phase oxidation of THF with air oxygen in the presence of a B_2O_3 catalyst [94]. The yield of α-hydroxytetrahydrofuran does not exceed 17%, whereas the yield of γ-butyrolactone reaches 75-80%.

γ-Hydroxy ketones are obtained in the oxidation of 2-alkyltetrahydrofurans [92], apparently as a result of decomposition of the corresponding hydroperoxides.

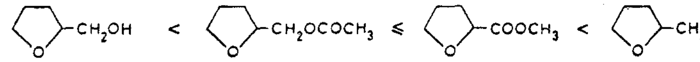
G. I. Nikishin and co-workers [95] have investigated the liquid-phase oxidation of monofunctional derivatives of THF – tetrahydrofurfuryl alcohol and its formate and acetate, as well as methyl tetrahydrofuran-2-carboxylate – with oxygen in the presence of manganese acetate as the catalyst. The chief reaction products are γ-butyrolactone and substituted γ-butyrolactone with a functional group in the γ position. Succinic acid, which is formed as a result of oxidation of the lactones to succinic anhydride and subsequent hydrolysis of the anhydride, was detected in the reaction products. Oxidation of the side chain leads to the formation of formic acid.



$R = CH_2OH, CH_2OOCH, CH_2OCOCH_3, COOCH_3$

Thus the oxidation of monofunctional derivatives of THF proceeds at two reaction centers, 2-C and 5-C. Ultraviolet irradiation substantially accelerates the oxidation process, and this makes it possible to carry out the reaction at lower temperatures.

The rate of oxidation of THF derivatives increases in the order [96]

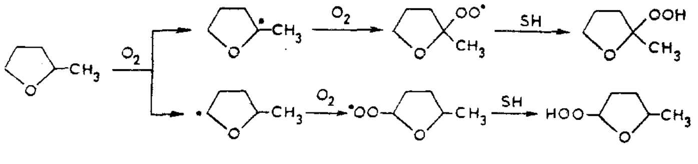


The lower rate of oxidation of tetrahydrofurfuryl alcohol as compared with the esters and 2-methyltetrahydrofuran is explained by the formation of hydrogen bonds between the hydroxyl groups and the peroxide radicals formed during the oxidation, which leads to a decrease in their reactivities.

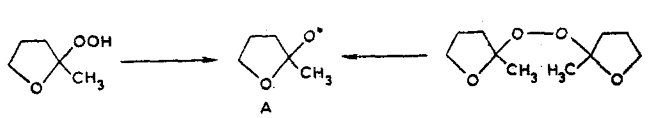
We obtained γ-butyrolactone, γ-hydroxymethyl-γ-butyrolactone (and its formate), and formic acid by liquid-phase oxidation of tetrahydrofurfuryl alcohol with air oxygen in the presence of B_2O_3 [97]. In the case of the liquid-phase oxidation of tetrahydrofurfuryl alcohol in the presence of B_2O_3, as well as B_2O_3 and cobalt acetate, the selectivity of the formation of γ-substituted γ-butyrolactones increases as compared with the selectivity of the oxidation in the presence of manganese acetate. This is due to the formation of more stable (with respect to subsequent oxidation) esters of boric acid and thereby to prevention of destruction of the five-membered ring.

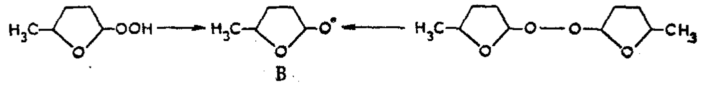
Whereas γ-butyrolactone and its derivatives are the principal reaction products in the oxidation of tetrahydrofurfuryl alcohol in the presence of salts of metals with variable valences and boron-containing catalysts, primarily tetrahydrofurancarboxylic acid (in up to 80 mole % yield) is formed in the liquid-phase oxidation of tetrahydrofurfuryl alcohol in the presence of Ag_2O and Ag_2O/Al_2O_3. Thus the oxidation of tetrahydrofurfuryl alcohol in the presence of heterogeneous catalysts is an extremely selective and convenient method for the preparation of tetrahydrofurancarboxylic acid. Liquid-phase oxidation of tetrahydrofurfuryl alcohol on a heterogeneous Ag_2O catalyst on carbon is carried out at low temperatures (50-60°) and low concentrations of the raw material in the reaction mixture [98]. The reaction is characterized by a high yield of tetrahydrofurancarboxylic acid (92%) and the absence of side products. The liquid-phase oxidation of tetrahydrofurfuryl alcohol and of other furan compounds with air oxygen on Pd on carbon has served as a model reaction in the study of the catalytic oxidation of hexoses to the corresponding carboxylic acids [99-101]. A disadvantage of this method for the synthesis of tetrahydrofurancarboxylic acid is the low efficiency of the formation of the desired product as a result of the high dilution of the reaction mixture.

M. A. Nadtochii [96] has made a detailed study of the liquid-phase oxidation of 2-methyltetrahydrofuran with oxygen with and without irradiation with UV light, as well as in the presence of solvents and salts of metals with variable valences. The oxidation proceeds via two pathways: via the methylidyne group in the 2 position and via the methylene group in the 5 position:

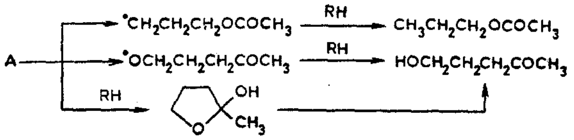


The hydroperoxide and peroxide subsequently undergo thermal decomposition:

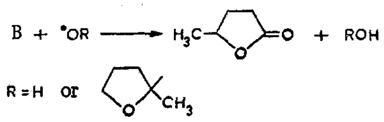




Radical A (and B) undergoes decyclization with subsequent detachment of a hydrogen atom from the solvent:



Radical B is primarily converted to γ-valerolactone:



Thus it follows from the literature data presented above that the liquid-phase oxidation of furan compounds, initiated by UV irradiation and salts of metals with variable valences as catalysts, differs substantially from the liquid-phase oxidation of furan compounds on heterogeneous catalysts with respect to the nature of the products, the selectivity of their formation, and the reaction mechanism. The selectivity of the formation of products of incomplete oxidation is considerably higher in the latter case than in the case of oxidation in the presence of salts of metals with variable valences. Whereas the liquid-phase oxidation of furan compounds in the presence of salts of metals with variable valences has a radical-chain mechanism, their liquid-phase oxidation on heterogeneous catalysts evidently proceeds via a mechanism of the nonradical type. The data on the mechanism of the oxidation of organic compounds on Ag_2O-containing catalysts [102] constitute evidence in favor of the latter.

On the basis of an analysis of the literature data on the vapor-phase and liquid-phase oxidation of furan compounds, it can be concluded that the liquid-phase oxidation of substituted furan compounds on heterogeneous catalysts (Ag_2O and Pd on carbon) and their vapor-phase oxidation on vanadium catalysts have much in common. In both cases one observes oxidation of the substituent to give furancarboxylic acids, which undergo decarboxylation under the conditions of vapor-phase oxidation. In the case of vapor-phase oxidation the heterogeneous process of formation of maleic anhydride is accompanied by homogeneous or heterogeneous-homogeneous oxidation of the furan compounds by molecular oxygen, which leads to inefficient consumption of the raw material as a result of the formation of volatile acids and resinous products. The latter, which are substances that are difficult to desorb at low temperatures and high concentrations of raw material, may lead to deactivation of the catalyst [47, 48]. A similar effect of a hydrogen donor (water) on the course of the process has been noted in vapor-phase and liquid-phase oxidation. The rate of oxidation of furan compounds by molecular oxygen decreases in the presence of water. The slowing down of oxidation of the aldehyde by water is associated with the fact that the advancing chain radical ($RCO_3^•$) forms a hydrogen bond with a water molecule, and the latter leads to a decrease in the activity of the peroxide radicals [102].

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ACYLATION OF DIBENZOFURAN WITH p-SUBSTITUTED BENZOYL CHLORIDES

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and Kh. Yu. Yuldashev

UDC 547.728:542.951.1

It is shown that benzoylation and p-chloro- and p-nitrobenzoylation of dibenzofuran in the presence of small amounts of $FeCl_3$, the $FeCl_3 \cdot CH_3NO_2$ complex, $ZnCl_2$, and acetylacetonatoiron lead to the production of the corresponding 3-acyldibenzofurans in high yields.

Reactions involving the acylation of heterocyclic compounds, particularly dibenzofuran, in the presence of $AlCl_3$ require the consumption of large amounts of the catalyst [1-4]. The use of 1.5 moles of anhydrous alu-

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[*] Deceased.

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