



# Selective oxidation of furfural in a bi-phasic system with homogeneous acid catalyst



Xiaodan Li, Xiaocheng Lan, Tiefeng Wang\*

Beijing Key Laboratory of Green Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

## ARTICLE INFO

### Article history:

Received 13 October 2015

Received in revised form

28 November 2015

Accepted 30 November 2015

Available online 11 January 2016

### Keywords:

Furfural

Catalytic oxidation

2(5H)-furanone

Solvent effect

Reaction network

## ABSTRACT

The selective catalytic oxidation of furfural to 2(5H)-furanone, succinic acid (SA) and maleic acid (MA) was studied. Under optimized conditions, furfural was oxidized to 2(5H)-furanone with a yield of 60–62% in an aqueous/organic bi-phasic system using 1,2-dichloroethane or ethyl acetate as the solvent and formic acid as the catalyst, while the total yield of SA and MA was 15–20%. Compared with other homogeneous and heterogeneous acid catalysts, formic acid gave a much higher selectivity to 2(5H)-furanone because it reacted with hydrogen peroxide to generate performic acid that had a strong oxidizing nature and good solubility in both the aqueous and organic phases. The solvent had a significant influence on the product distribution. A simplified reaction network was established to quantitatively analyze the solvent effect based on the reaction rate constants. In the homogeneous system, the yield of 2(5H)-furanone decreased while the yield of SA increased with an increasing dielectric constant of the solvent. The formic acid/furfural molar ratio, reaction temperature and furfural concentration were optimized for the selective oxidation of furfural to 2(5H)-furanone in the bi-phasic reaction system.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

With increasing consumption of energy and diminishing supply of fossil fuels, substantial interest has been devoted to search for renewable energy resources in the world. In this respect, biomass, which is renewable, environmental-friendly, abundant and widespread, is considered to be an ideal substitute for traditional fossil fuels [1–4]. In recent years, various catalytic conversion strategies have been developed for the conversion of biomass to bio-based platform compounds, which can be further converted to a wide range of target products [5–9]. Among these renewable platform compounds, furfural, produced by hydrolysis and dehydration of xylan contained in hemicellulose, is one of the most important building blocks for bio-refinery [10–12]. Catalytic oxidation has been used to convert furfural to many chemical intermediates and end products, including furanone, furoic acid, fumaric acid (FA), succinic acid (SA) and maleic acid (MA) [6,13–18]. Most of the current studies focus on the selective oxidation of furfural to diacids or acid anhydrides, especially to SA, MA and maleic anhydride. However, the studies on the oxidation of furfural to 2(5H)-furanone are very limited.

Furanone can be synthesized by deoxygenation of substituted butanoic acids at high temperature, transformation of hydroxybutyrolactones with acids or amines, hydrolysis of 2-methoxyfuran and cyclocarbonylation of terminal alkynols in the presence of palladium [19–22]. Nevertheless, the above methods are deficient owing to their expensive reagents, complicated processes, extreme reaction conditions and low yield. Currently, 2(5H)-furanone is mainly produced by furfural oxidation. Badovskay [23] reported the oxidation of furfural to 2(5H)-furanone with a yield of 25% by autocatalysis, and the yield was not significantly improved in the presence of Mo (VI) or Cr (VI). Cao et al. [13], found that when the autocatalytic oxidation of furfural was carried out in a bi-phasic system using dichloroethane as the solvent, a 37% yield of 2(5H)-furanone was obtained, however the reaction time was longer than 10 hours. Poskonin [24] reported the synthesis of 2(5H)-furanone from furfural in water using niobium (V) acetate tetrahydrate as the catalyst and hydrogen peroxide as the oxidant, but more than 80 hours were needed to obtain a 60% yield. Despite decades of study, problems with furfural oxidation to 2(5H)-furanone still exist in the moderate yield (30–50%), long reaction time and the use of chlorinated solvents. The main utility of 2(5H)-furanone at present is limited to the intermediate for the synthesis of biologically active natural products [25].

2(5H)-Furanone is an ideal material for the production of lactones and diols in terms of its chemical structure. In our previous

\* Corresponding author.

E-mail address: [wangtf@tsinghua.edu.cn](mailto:wangtf@tsinghua.edu.cn) (T. Wang).

work, 2(5H)-furanone was hydrogenated to  $\gamma$ -butyrolactone (GBL) with a high yield using supported metal catalysts [26]. The use of 2(5H)-furanone as the intermediate for the conversion of furfural to C4 lactones and diols can improve the atom economy of the conversion path and reduce the cost caused by harsh conditions, in comparison with other biomass-derived intermediates like diacids and acid anhydrides. Thus, the highly selective oxidation of furfural to 2(5H)-furanone can provide a better approach to produce C4 lactones and diols from furfural, which have been widely used in the fields of medicine, chemical, plastics, electric and others [27,28]. Hydrogen peroxide is usually used as the oxidant for furfural oxidation to 2(5H)-furanone, because the non-catalytic polymerization of furfural is severe when furfural interacts with molecular oxygen [29]. The control of selectivity is a great challenge for furfural oxidation to 2(5H)-furanone, as many side reactions including non-catalytic polymerization, oxidation to diacids and deep oxidation may occur.

In this work, different acid catalysts were evaluated for the oxidation of furfural to 2(5H)-furanone in both the bi-phasic and homogeneous systems. A simplified reaction network was established, and the reaction rate constants and apparent activation energies were calculated to analyze the solvent effect. The solvent effect was investigated in homogeneous, bi-phasic and tri-phasic systems using a variety of solvents with different polarities. The product distribution was correlated with the solvent property to guide the selection of solvent for improved yield of 2(5H)-furanone. Additionally, the effects of the formic acid/furfural molar ratio, reaction temperature and furfural concentration were studied in detail.

## 2. Materials and methods

### 2.1. Materials

Methanol, tetrahydrofuran, tetrachloromethane, benzene, toluene, cyclohexane, iso-octane, *n*-heptane, ethyl acetate, sulfuric acid (98%), phosphoric acid (85%) and sodium sulfate were all of analytical grade and purchased from Beijing Chemical Works. Isopropanol (SCR Beijing, 99.5%), 1,2-dichloroethane (J&K Chemical, 99%),  $\gamma$ -butyrolactone (Xiya Reagent, 99%), formic acid (SCR Beijing, 88%) and hydrogen peroxide (Beijing Modern Oriental Fine Chemistry Co., Ltd., 30%) were purchased. The above reagents were used without further purification. Furfural (SCR Beijing, 99%) was purified by vacuum distillation before use. The strong acid ion exchange resin Amberlyst-15 was purchased from Aladdin Industrial Corporation, and ZrTiO<sub>4</sub> was prepared according to the literature [30]. The corresponding precursors were co-precipitated to synthesize Ti(OH)<sub>4</sub>-Zr(OH)<sub>4</sub>, and this hydroxide was calcined at 923 K to obtain ZrTiO<sub>4</sub>.

### 2.2. Oxidation reaction

#### 2.2.1. Oxidation of furfural

All the furfural oxidation reactions were carried out in a three-necked flask of 50 mL, equipped with a condenser to reduce volatilization loss of the solvent. An oil bath was used to control the reaction temperature. In a typical experiment, 10 mL of solvent, 1.5 mL of distilled water, 4.0 g of furfural, 4.0 g of sodium sulfate and an appropriate amount of acid catalyst were added to the flask and heated to the reaction temperature. When the reaction mixture reached the set temperature, 10 mL of hydrogen peroxide (30%) was added to the reactor dropwise during the first hour while stirring. The reaction mixture was sampled and analyzed by a gas chromatograph (GC) and a high performance liquid chromatograph (HPLC).

#### 2.2.2. Oxidation of 2(5H)-furanone

The oxidation of 2(5H)-furanone was carried out in a similar apparatus to that for the oxidation of furfural. For each experiment, 4.0 g of 2(5H)-furanone was dissolved in 10 mL of 1,2-dichloroethane, then 1.5 mL of formic acid and 1.5 mL of distilled water were added to the mixture. When the reaction temperature reached the set value, 10 mL of hydrogen peroxide was added dropwise to the mixture during the first hour while stirring. The reaction mixture was sampled and analyzed by GC and HPLC.

### 2.3. Analytical methods

Gas chromatograph (GC 7900 II, Techcomp Instrument Company) equipped with a super-wax capillary column (30 m × 0.25 mm × 0.5  $\mu$ m) and an FID detector was used to analyze the contents of furfural and 2(5H)-furanone in the reaction mixture. The diacids including SA and MA were analyzed with a Shimadzu 10 AT-VP HPLC equipped with a C18 column (150 mm × 4.6 mm) and a UV detector. For HPLC measurement, the samples were diluted 500 times with distilled water; The mobile phase was methanol with distilled water (3/97, v/v) containing KH<sub>2</sub>PO<sub>4</sub> (0.02 mol/L), and its pH was adjusted to 2.75 by H<sub>3</sub>PO<sub>4</sub>; The flow rate was fixed at 1.0 mL/min and the temperature of the column was kept at 303 K; The injection volume was 20  $\mu$ L.

The conversion of furfural and the selectivity and yield of products are calculated as follows:

$$\text{Furfural conversion (\%)} = \frac{(n_{\text{fur}}^0 - n_{\text{fur}})}{n_{\text{fur}}^0} \times 100 \quad (1)$$

$$\text{Product selectivity (\%)} = \frac{n_{\text{pro}}}{(n_{\text{fur}}^0 - n_{\text{fur}})} \times 100 \quad (2)$$

$$\text{Product yield (\%)} = \frac{n_{\text{pro}}}{n_{\text{fur}}^0} \times 100 \quad (3)$$

where  $n_{\text{fur}}^0$  is the initial mole quantity of furfural loaded into the reactor, and  $n_{\text{fur}}$  and  $n_{\text{pro}}$  are the moles of furfural and products, respectively. The mole quantity of each component  $n_i$  in the homogeneous system and bi-phasic system was calculated based on Eq. (4) and Eq. (5), respectively:

$$n_i = C_i \times V \quad (4)$$

where  $C_i$  is the concentration of the component measured by GC or HPLC, and  $V$  is the volume of the reaction mixture at a given time.

$$n_i = C_{i,\text{aq}} \times V_{\text{aq}} + C_{i,\text{or}} \times V_{\text{or}} \quad (5)$$

where  $C_{i,\text{aq}}$  and  $C_{i,\text{or}}$  refer to the concentration of the component in the aqueous and organic phases, respectively, and  $V_{\text{aq}}$  and  $V_{\text{or}}$  refer to the volume of the aqueous and organic phases at a given time, respectively.

## 3. Results and discussion

### 3.1. Homogeneous and heterogeneous acid catalysts

The furfural oxidation reaction was first studied in a bi-phasic system with 1,2-dichloroethane as the solvent and in a homogeneous system with methanol as the solvent, focusing on the effect of acid catalysts. The results are shown in Fig. 1. Among the selected homogeneous catalysts, formic acid had the best performance for furfural oxidation to 2(5H)-furanone in both the bi-phasic and homogeneous systems. The yield of 2(5H)-furanone reached 60.3% in the bi-phasic system, while it decreased to 13.1% in the homogeneous system. When inorganic acid, H<sub>3</sub>PO<sub>4</sub> or H<sub>2</sub>SO<sub>4</sub>, was used as the catalyst, the yield of 2(5H)-furanone was lower than 10% in both the bi-phasic and homogeneous systems. For heterogeneous

Download English Version:

<https://daneshyari.com/en/article/4757407>

Download Persian Version:

<https://daneshyari.com/article/4757407>

[Daneshyari.com](https://daneshyari.com)