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## Article

# Oxidation of styrene to benzaldehyde by *p*-toluenesulfonic acid using hydrogen peroxide in the presence of activated carbon



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## ABSTRACT

The selective oxidation of styrene to benzaldehyde catalyzed by *p*-toluenesulfonic acid (*p*-TsOH) in the presence of activated carbon (AC) was investigated with H<sub>2</sub>O<sub>2</sub> as the oxidant. The reaction parameters of reaction time, temperature, catalyst mass, and styrene/H<sub>2</sub>O<sub>2</sub> molar ratios were evaluated. A strong promoting effect of AC on the *p*-TsOH/H<sub>2</sub>O<sub>2</sub> system was observed. The appropriate ratio and amounts of AC and *p*-TsOH were an important factor. The acidity of *p*-TsOH does not play a significant role. *p*-TsOH reacted with H<sub>2</sub>O<sub>2</sub> by a non-radical process to oxidize styrene. The function of the AC was to activate H<sub>2</sub>O<sub>2</sub> and to help the *p*-TsOH/H<sub>2</sub>O<sub>2</sub> system in styrene oxidation. The reduction of oxygen containing groups (-OH, -COOH) on AC by a high temperature treatment or introduction of -SO<sub>3</sub>H groups onto AC affected the styrene conversion. The -SO<sub>3</sub>H groups were more effective than the oxygen-containing groups on the AC in promoting styrene oxidation.

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## 1. Introduction

The selective oxidation of styrene to benzaldehyde can be carried out by using atmospheric oxygen [1,2], alkyl hydroperoxides [3,4], or H<sub>2</sub>O<sub>2</sub> [5–9] in the presence of an appropriate metal-based catalyst to activate the oxidant. The use of H<sub>2</sub>O<sub>2</sub> to oxidize styrene produces different products, depending upon the catalyst and the reaction conditions. H<sub>2</sub>O<sub>2</sub> combined with a catalyst can provide hydroxyl radicals ( $\cdot\text{OH}$ ).  $\cdot\text{OH}$  can attack styrene by electrophilic addition to the multiple C–C bonds and aromatic rings [10,11].

Recently, some carbon or silica supported sulfonic acid were prepared and used as a solid acid catalyst in many reactions [12–15]. Using H<sub>2</sub>O<sub>2</sub> as an oxidant, the solid acid catalysts (supported sulfonic acid) as a metal-free catalyst selectively oxidized organic compounds. For example, Maggi et al. [12] developed silica- and polystyrene-supported sulfonic acids as a

metal-free heterogeneous catalyst for the oxidation of hydroquinones to the corresponding 1,4-benzoquinones with H<sub>2</sub>O<sub>2</sub>. Yang et al. [16] investigated sulfonated carbon as a catalyst for the oxidation of aldehydes to the corresponding acids by H<sub>2</sub>O<sub>2</sub>. Sato et al. [17] reported a procedure for the synthesis of 1,2-diols by the dihydroxylation of olefins with H<sub>2</sub>O<sub>2</sub> catalyzed by resin-supported sulfonic acid.

*p*-Toluenesulfonic acid (*p*-TsOH) as a catalyst has shown successful results in some acid-catalyzed reactions [18–21]. *p*-TsOH contains a sulfonic acid group (-SO<sub>3</sub>H), and dissolves easily in water and is insoluble in organic reagents such as benzene, toluene, and alkanes. Thus, *p*-TsOH can be recycled by separating the organic phase and aqueous phase. Very recently, Rostami et al. [22] researched the selective oxidation of sulfides to sulfoxides using H<sub>2</sub>O<sub>2</sub> catalyzed by *p*-TsOH under solvent-free conditions.

In order to extend the method of the selective oxidation of

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styrene, we evaluated the activity of *p*-TsOH as a metal-free catalyst for the oxidation of styrene to benzaldehyde with H<sub>2</sub>O<sub>2</sub> as oxidant in the presence of activated carbon (AC). A strong promoting effect of AC on the *p*-TsOH/H<sub>2</sub>O<sub>2</sub> system was observed. Investigating the interaction of *p*-TsOH and AC in the oxidation reaction will be helpful for understanding the reaction mechanism of solid acid catalysts in similar reaction systems.

## 2. Experimental

### 2.1. Chemicals

All chemicals used for the experiments were AR grade, including AC, HNO<sub>3</sub> (65%), H<sub>2</sub>SO<sub>4</sub> (98%), and *p*-TsOH. These were obtained from Tianjin Kermel Chemical Reagents Company. Styrene (AR) and H<sub>2</sub>O<sub>2</sub> (30%) were supplied by Sinopharm Chemical Reagents Company.

### 2.2. AC pretreatment

Commercial AC was first boiled in deionized water for 2 h, and then washed with deionized water. The washed AC was treated with 65% HNO<sub>3</sub> at room temperature for 24 h. After filtration, the acid-treated AC was washed thoroughly by deionized water and then dried at 105 °C overnight, and labeled as HAC. HAC was treated in a N<sub>2</sub> or 5% H<sub>2</sub>/Ar atmosphere by heating at a rate of 10 °C/min to 800 °C, and then kept at this temperature for 6 h. The samples are denoted as HAC<sub>N2</sub> and HAC<sub>H2</sub>.

In addition, HAC (1 g) was heated in 100 mL concentrated H<sub>2</sub>SO<sub>4</sub> (98%) at 150 °C for 15 h under N<sub>2</sub> atmosphere. The resulting carbon material was washed with hot distilled water (> 80 °C) until no sulfate ions were detected in the wash water. The resulting material was designated as HAC-SO<sub>3</sub>H. The S content of the sample was 5.5 mmol/g, which was determined by X-ray fluorescence (Siemens SRS3400).

### 2.3. AC characterization

X-ray diffraction (XRD) analysis was performed on a Rigaku D8 Advance diffractometer with Cu K<sub>α</sub> radiation, voltage 40 kV and current 40 mA. Fourier transform infrared (FT-IR) spectra were recorded in the range of 400–4000 cm<sup>-1</sup> on a Bruker Tensor 27 spectrometer. The total acid content of the AC was obtained using a standard acid-base titration [23]. For a typical titration experiment, an AC sample mass of 0.5 g was suspended in 25 mL standard NaOH solution (0.1 mol/L) and shaken in a closed container for 24 h. The slurry was filtered to remove AC. An aliquot of 10 mL was back-titrated with 0.1 mol/L HCl.

### 2.4. Styrene oxidation

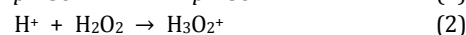
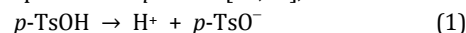
The oxidation experiments were carried out in a 50-mL glass reactor with magnetic stirring immersed in a water recirculating bath and equipped with a reflux condenser. A standard run is as follows: an amount of HAC or *p*-TsOH, 5 mL

of acetonitrile, and styrene and H<sub>2</sub>O<sub>2</sub> in proportion were added to the reactor and stirred by a magnetic stirrer at the set temperature for a set time. After the reaction, the products were analyzed using an Agilent-6890 gas chromatograph equipped with a FID using a HP-5 capillary column (30 m × 0.32 mm × 0.25 μm) and N<sub>2</sub> as the carrier gas. The internal standard method was adopted for the quantitative analysis of the products using toluene as an internal standard substance. The conversion of styrene (*C*<sub>styrene</sub>) and selectivity for benzaldehyde (*S*<sub>benzaldehyde</sub>) was defined as follows:  $C_{\text{styrene}} = (n_0 - n_{\text{styrene}})/n_0 \times 100\%$ ;  $S_{\text{benzaldehyde}} = n_{\text{benzaldehyde}}/(n_0 - n_{\text{styrene}}) \times 100\%$ . *n*<sub>0</sub> and *n*<sub>styrene</sub> denoted the initial mole number and the final mole number.

## 3. Results and discussion

### 3.1. Reaction conditions

We used *p*-TsOH as the catalyst for the selective oxidation of styrene to benzaldehyde with H<sub>2</sub>O<sub>2</sub> as an oxidant in the presence of AC. In the preliminary study without styrene, no benzaldehyde was formed using either the *p*-TsOH/H<sub>2</sub>O<sub>2</sub> or the *p*-TsOH/HAC/H<sub>2</sub>O<sub>2</sub> system. The reaction parameters were first optimized for the oxidation of styrene. The results are summarized in Table 1. With 0.058 mmol of *p*-TsOH as catalyst and 3.5 molar ratio of H<sub>2</sub>O<sub>2</sub>/styrene at 60 °C, the styrene conversion was very low, 8.7% after 5 h of reaction (Table 1, entry 1). The low activity was attributable to H<sub>2</sub>O<sub>2</sub> protonation to form an oxonium ion in the presence of *p*-TsOH [22,24],



which enhanced H<sub>2</sub>O<sub>2</sub> stability and reduce its reactivity. When AC treated by HNO<sub>3</sub> (HAC) was added into the *p*-TsOH/H<sub>2</sub>O<sub>2</sub> system, the styrene conversion increased. For example, the styrene conversion and benzaldehyde selectivity were 35.3% and 85.4%, respectively, when 10 mg HAC was added, and they were 43.3% and 86.8%, respectively, when adding 50 mg HAC (Table 1, entries 2 and 3). The results showed that the addition

**Table 1**

Oxidation of styrene to benzaldehyde with H<sub>2</sub>O<sub>2</sub> catalyzed by HAC and *p*-TsOH under different conditions.

Entry	HAC (mg)	<i>p</i> -TsOH (mmol)	H <sub>2</sub> O <sub>2</sub> /styrene (mol/mol)	Temperature (°C)	<i>C</i> <sub>styrene</sub> (%)	<i>S</i> <sub>benzaldehyde</sub> (%)
1	0	0.058	3.5	60	8.7	90.1
2	10	0.058	3.5	60	35.3	85.4
3	50	0.058	3.5	60	43.3	86.8
4	10	0	3.5	60	3.0	90.3
5	10	0.29	3.5	60	53.5	81.5
6	50	0.29	3.5	60	80.1	86.5
7	100	0.58	3.5	60	> 99	53.2
8	10	0.058	3.5	40	13.6	87.0
9	10	0.058	3.5	50	21.2	86.3
10	10	0.058	3.5	80	68.2	71.7
11	10	0.058	2.5	60	14.1	89.2
12	10	0.058	4.0	60	35.8	83.0
13	10	0.058	4.5	60	37.0	80.1
14*	10	0.058	4.5	60	38.3	82.0

Reaction conditions: styrene 5 mmol, acetonitrile 5 mL, 5 h.

\* Using recycling HAC.

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