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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 H₂O₂ as the oxidant. The reaction parameters of reaction time, temperature, catalyst mass, and styrene/H₂O₂ molar ratios were evaluated. A strong promoting effect of AC on the *p*-TsOH/H₂O₂ 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 H₂O₂ by a non-radical process to oxidize styrene. The function of the AC was to activate H₂O₂ and to help the *p*-TsOH/H₂O₂ system in styrene oxidation. The reduction of oxygen containing groups (–OH, –COOH) on AC by a high temperature treatment or introduction of –SO₃H groups onto AC affected the styrene conversion. The –SO₃H 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 H₂O₂ [5–9] in the presence of an appropriate metal-based catalyst to activate the oxidant. The use of H₂O₂ to oxidize styrene produces different products, depending upon the catalyst and the reaction conditions. H₂O₂ combined with a catalyst can provide hydroxyl radicals (•OH). •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 H₂O₂ 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 H₂O₂. Yang et al. [16] investigated sulfonated carbon as a catalyst for the oxidation of aldehydes to the corresponding acids by H₂O₂. Sato et al. [17] reported a procedure for the synthesis of 1,2-diols by the dihydroxylation of olefins with H₂O₂ 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 (–SO₃H), 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 H₂O₂ 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 H₂O₂ as oxidant in the presence of activated carbon (AC). A strong promoting effect of AC on the *p*-TsOH/H₂O₂ 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, HNO₃ (65%), H₂SO₄ (98%), and *p*-TsOH. These were obtained from Tianjin Kermel Chemical Reagents Company. Styrene (AR) and H₂O₂ (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% HNO₃ 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 N₂ or 5%H₂/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_{N2} and HAC_{H2}.

In addition, HAC (1 g) was heated in 100 mL concentrated H₂SO₄ (98%) at 150 °C for 15 h under N₂ 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-SO₃H. 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_α radiation, voltage 40 kV and current 40 mA. Fourier transform infrared (FT-IR) spectra were recorded in the range of 400–4000 cm⁻¹ 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 H₂O₂ 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 N₂ 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*_{styrene}) and selectivity for benzaldehyde (*S*_{benzaldehyde}) was defined as follows: *C*_{styrene} = (*n*₀ − *n*_{styrene})/*n*₀ × 100%; *S*_{benzaldehyde} = *n*_{benzaldehyde}/(*n*₀ − *n*_{styrene}) × 100%. *n*₀ and *n*_{styrene} 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 H₂O₂ as an oxidant in the presence of AC. In the preliminary study without styrene, no benzaldehyde was formed using either the *p*-TsOH/H₂O₂ or the *p*-TsOH/HAC/H₂O₂ 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 H₂O₂/styrene at 60 °C, the styrene conversion was very low, 8.7% after 5 h of reaction (Table 1, entry1). The low activity was attributable to H₂O₂ protonation to form an oxonium ion in the presence of *p*-TsOH [22,24],

which enhanced H₂O₂ stability and reduce its reactivity. When AC treated by HNO₃ (HAC) was added into the *p*-TsOH/H₂O₂ 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 H₂O₂ catalyzed by HAC and *p*-TsOH under different conditions.

Entry	HAC (mg)	<i>p</i> -TsOH (mmol)	H ₂ O ₂ /styrene (mol/mol)	Temperature (°C)	<i>C</i> _{styrene} (%)	<i>S</i> _{benzaldehyde} (%)
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.

of HAC into the *p*-TsOH/H₂O₂ system increased the styrene conversion.

Carbon as a catalyst has been used in several processes for the oxidation of organic compounds in liquid using H₂O₂ as the oxidant [25–27]. When using only 10 mg HAC as catalyst, the conversion of styrene was very low, and was 3% after 5 h of reaction (Table 1, entry 4).

It is generally thought that the interaction of AC with H₂O₂ generates free radical species ($\cdot\text{OH}/\cdot\text{OOH}$) according to the following reaction, Eqs. (3) and (4) [11,27,28].

The free radical species directly oxidize styrene to form the oxidation products.

It is important to note that when using HAC as catalyst, some O₂ was formed by H₂O₂ decomposition in the solution of styrene, acetonitrile, H₂O₂, and HAC (Fig. 4). The formation of O₂ was attributed to the interaction between the free radical species according to the reaction Eq. (5) [11,12,29].

Thus, the low activity over HAC implied that the reaction between the free radical species and styrene was the rate determining step. The faster reaction between the free radicals generates more O₂, while part of the H₂O₂ was consumed.

When the amount of HAC was fixed (10 mg), and the amount of *p*-TsOH was increased from 0.058 to 0.29 mmol, after 5 h of reaction, the corresponding styrene conversion increased from 35.3% to 53.5% while the benzaldehyde selectivity only decreased from 85.4% to 81.5%. When simultaneously increasing the amounts of both HAC and *p*-TsOH to 50 mg and 0.29 mmol, respectively, a significantly promotion of styrene oxidation was observed. The styrene conversion was increased to 80.1% and the benzaldehyde selectivity was 86.5% (Table 1, entry 6). On further increasing both HAC and *p*-TsOH to 100 mg and 0.58 mmol, respectively, the styrene conversion increased to > 99%, and the selectivity for benzaldehyde decreased to 53.2%. These results indicated that the appropriate ratio and amount of HAC and *p*-TsOH were an important factor for obtaining high activity and selectivity in styrene oxidation.

For the 10 mg HAC and 0.058 mmol *p*-TsOH system, when increasing the reaction temperature from 40 to 80 °C, the styrene conversion increased remarkably from 13.6% to 68.2%. The benzaldehyde selectivity decreased from 87% to 71.7%, and the corresponding benzoic acid selectivity was gradually increased. Thus, increasing the reaction temperature can improve the oxidation ability of the *p*-TsOH/HAC/H₂O₂ system. At 60 °C, when increasing the molar ratios of H₂O₂/styrene from 2.5 to 3.5, the styrene conversion increased from 14.1% to 35.3%. With further increasing of the molar ratio to 4.5, the styrene conversion was almost unchanged (Table 1, entries 2 and 13). This indicated that when the amount of catalyst and reaction temperature were fixed, excess H₂O₂ could not be effectively activated. Moreover, after the reaction, the HAC was filtrated, washed, dried, and used again. The styrene conversion and benzaldehyde selectivity with the HAC used/*p*-TsOH/H₂O₂ were almost equal to those of fresh HAC (Table 1, entries 13 and 14).

3.2. Effect of the surface groups of the AC

To explore the effect of the carbon surface chemistry on the oxidation reaction, the styrene oxidation was catalyzed by a high temperature treated HAC (HAC_{H2} and HAC_{N2}) or untreated HAC, and *p*-TsOH. The results are shown in Fig. 1. When using 50 mg HAC as catalyst, the conversion of styrene was very low (8.5%, 10 h). Similarly, with the heat-treated HAC (50 mg) as catalyst, the conversion of styrene was still low. After 10 h of reaction, the conversion of styrene and the selectivity for benzaldehyde were 4% and 95% for HAC_{H2} and 5% and 86% for HAC_{N2}, respectively.

When using only 0.29 mmol *p*-TsOH as catalyst, the conver-

Fig. 1. Oxidation of styrene to benzaldehyde using different catalysts. (a) HAC/*p*-TsOH; (b) HAC_{H2}/*p*-TsOH; (c) HAC_{N2}/*p*-TsOH. (1) Styrene conversion with AC; (2) Benzaldehyde selectivity with AC; (3) Styrene conversion with AC/*p*-TsOH; (4) Benzaldehyde selectivity with AC/*p*-TsOH; (5) Styrene conversion with *p*-TsOH; (6) Benzaldehyde selectivity with *p*-TsOH. Reaction conditions: AC 50 mg, *p*-TsOH 0.29 mmol, styrene 5 mmol, acetonitrile 5 mL, H₂O₂/styrene molar ratio 3.5, 60 °C, 10 h.

sion of styrene also was very low (11%, 10 h) (Fig. 1(a)). With the simultaneous use of *p*-TsOH and heat-treated HAC as catalyst, compared with HAC (89% styrene conversion and 80% benzaldehyde selectivity), the conversion of styrene was further increased to 94% for HAC_{H2} and 97% for HAC_{N2}. The corresponding selectivity for benzaldehyde decreased to 57% and 61% after 10 h of reaction, respectively. More benzoic acid was observed, implying that styrene was over-oxidized.

The three different AC (HAC, HAC_{H2}, and HAC_{N2}) were characterized to investigate the surface and structure. For HAC and heat-treated HAC, the XRD patterns exhibited similar diffraction peaks at $2\theta = 10^\circ$ – 60° . All the three sample frameworks were amorphous (Fig. 2(a)) [30]. The FT-IR spectra of HAC and heat-treated HAC are shown in Fig. 2(b). For the HAC sample, it displayed O–H stretches (3654 cm^{-1}), C=O stretches (1708 cm^{-1}), C=C stretches (1594 cm^{-1}), and C–O stretches (1000 – 1200 cm^{-1}) [31,32]. After HAC was heat-treated in H₂/Ar or N₂ at 800 °C, remarkable decrease of the bands at 3654 and 1000 – 1200 cm^{-1} were observed. The results indicated that the oxygen-containing groups on the carbon surface were decreased by the high temperature treatment of HAC, in agreement with literature reports [29,33]. The total acidity of the AC was obtained using a standard acid-base back titration [23]. The total acidity were 0.239 mmol/g for HAC, 0.087 mmol/g for HAC_{H2}, and 0.099 mmol/g for HAC_{N2}. The decrease in the total acidity was attributed to the reduction of the oxygen-containing groups by the high temperature treatment of AC, which was consistent with the FT-IR results. The decrease in the amount of the oxygen-containing groups was very beneficial for the decomposition of H₂O₂ [29,33] and more •OH radicals were formed, which in turn increased the styrene conversion, and reduced the corresponding selectivity for benzaldehyde for the HAC_{H2} or HAC_{N2} and *p*-TsOH systems.

The •OH formed in the H₂O₂ system can be probed using a method described previously [34]. It is known that •OH reacts with terephthalic acid (TA) in basic solution to generate TAOH, which emits a unique fluorescence signal with its peak centered at 427 nm. Figure 3 shows the comparison of the fluorescence intensity for different samples illuminated for a fixed time (30 min) with pure H₂O₂ as the reference. It was obvious that the

Fig. 3. Fluorescence spectra of TAOH formed by the reaction of TA with •OH radicals generated by different samples under visible light irradiation for 30 min.

fluorescence intensity was proportional to the amount of produced hydroxyl radicals. The amount of •OH produced on the heat-treated HAC was more than that of the •OH produced on HAC. This also agreed with their catalytic activities for H₂O₂ decomposition and styrene conversion. For the *p*-TsOH and HAC_{H2} system, the formation of •OH was inhibited, suggesting that the mechanism of H₂O₂ decomposition was changed in the presence of *p*-TsOH.

There were oxygen-containing groups (such as –OH, –COOH) on the surface of HAC and the –SO₃H groups of *p*-TsOH in the *p*-TsOH/HAC system. To determine which of the oxygen-containing groups or –SO₃H plays a leading role, HAC was heated in concentrated H₂SO₄ to introduce sulfate acid groups (–SO₃H) [15]. This was labeled HAC-SO₃H. After the sulfonation treatment of HAC, hydrophilic groups (–SO₃H, –COOH, –OH) coexist on the surface of the HAC-SO₃H sample [35]. With HAC-SO₃H as the catalyst, the conversion of styrene and selectivity for benzaldehyde were 64.8% and 80.6%, respectively, which were significantly higher than those when using only HAC as the catalyst under the same reaction conditions. This

Fig. 2. XRD patterns (a) and FT-IR spectra (b) of HAC (1), HAC_{H2} (2), and HAC_{N2} (3).

showed that the SO_3H group was much more effectively than the oxygen-containing groups for promoting the oxidation of styrene using H_2O_2 as oxidant.

3.3. Amount of H_2O_2 in the p -TsOH/HAC system

Both styrene oxidation and H_2O_2 decomposition proceeded simultaneously in styrene oxidation process and the contribution to the gas volume was measured in the reaction solution. Figure 4 demonstrates the kinetic oxygen evolution curves with different H_2O_2 systems. When styrene, acetonitrile, and H_2O_2 were mixed and stirred at 60 °C, a small amount of oxygen evolution was observed, which was attributed to H_2O_2 decomposition by the heating and stirring of the solution. An hour later, the reaction achieved equilibrium. When 0.29 mmol of p -TsOH was added into the above mixture, no further decomposition of H_2O_2 was observed. Some O_2 was produced by adding 50 mg HAC into the mixture of styrene, acetonitrile, and H_2O_2 . AC acts as an initiator for the decomposition of H_2O_2 , yielding free radical species such as $\cdot\text{OH}$ in solution [11,12,29,33]. These results are in agreement with the fluorescence results. Given the poor catalytic activity observed when using only HAC as catalyst, the free radicals from the HAC reaction with H_2O_2 cannot effectively oxidize styrene. When 50 mg of HAC and 0.29 mmol p -TsOH were simultaneously added into the mixture of styrene, acetonitrile, and H_2O_2 , compared to the addition of only 50 mg of HAC, the amount of O_2 evolved slightly decreased, but was higher than that using only 0.29 mmol p -TsOH. Combining with the data of styrene oxidation, the free radicals species formed by HAC was more conducive to the styrene oxidation through promoting the p -TsOH/ H_2O_2 system.

For the system of 50 mg HAC and 0.29 mmol p -TsOH, the amount of H_2O_2 decomposition calculated by the volume of generated O_2 and the amount of residual H_2O_2 measured by the iodometric method after reaction are shown in Table 2. The

Fig. 4. Kinetics curves of O_2 produced by the decomposition of H_2O_2 in the different reaction systems. (1) Mixture of acetonitrile, styrene, and H_2O_2 ; (2) Acetonitrile, styrene, p -TsOH, and H_2O_2 ; (3) Acetonitrile, styrene, p -TsOH, HAC, and H_2O_2 ; (4) Acetonitrile, styrene, HAC, and H_2O_2 . Reaction conditions: HAC 50 mg, p -TsOH 0.29 mmol, styrene 5 mmol, acetonitrile 5 mL, molar ratio of H_2O_2 /styrene 3.5, 60 °C.

Table 2

Amounts of H_2O_2 in different catalyst systems.

Catalyst system	H_2O_2 decomposition (%)	Residual H_2O_2 (%)	Reactive H_2O_2 (%)
HAC/ p -TsOH	8.4	7.9	79.9
HAC	10.8	20.7	65.8
HAC_{N_2} / p -TsOH	7.1	6.8	81.6
HAC_{N_2}	14.5	22.4	63.1
HAC_{H_2} / p -TsOH	6.2	4	89.8
HAC_{H_2}	16.1	23.5	60.4

Reaction conditions: p -TsOH 0.29 mmol, HAC (HAC_{H_2} , or HAC_{N_2}) 50 mg, acetonitrile 5 mL, styrene 5 mmol, H_2O_2 /styrene molar ratio 3.5, 60 °C, 10 h.

amount of H_2O_2 decomposition in the p -TsOH/HAC system was less than that of the with only HAC system. This may be due to the presence of p -TsOH, which acidified the reaction mixture and partially inhibited the decomposition of H_2O_2 . The amount of residual H_2O_2 in the p -TsOH/HAC system also was less than that in the HAC system. Therefore, more H_2O_2 participated in the oxidation of styrene in the p -TsOH/HAC/ H_2O_2 system.

Compared with HAC and heat-treated HAC, the latter showed better activity for the decomposition of H_2O_2 (Table 2). The amounts of H_2O_2 decomposition increased in the following order: $\text{HAC}_{\text{H}_2} > \text{HAC}_{\text{N}_2} > \text{HAC}$. The better decomposition of H_2O_2 was attributed to the presence of a higher amount of basic surface groups (formed by the high temperature treatment of AC) that can interact with H_2O_2 to donate one electron, which resulted in the formation of $\cdot\text{OH}$ and further formation of O_2 [11,12,24]. The increased $\cdot\text{OH}$ formed by the heat-treated HAC facilitated styrene conversion, but decreased the selectivity for benzaldehyde with reaction time.

3.4. Effect of acidity and free radical scavenger

Reaction mechanisms in the liquid phase are generally more complex, and may involve a combination of homogeneous and heterogeneous reaction steps. On the basis of previously reported mechanisms on the catalytic application of acids in the oxidation of organic compounds using H_2O_2 [17,36–38], one explanation is that p -TsOH acts as a protic acid, which polarizes the O–O bond in H_2O_2 through hydrogen bonding to produce the reactive oxygen transfer agent. Another possible explanation is the in situ formation of peroxysulfonic acid by the reaction of p -TsOH with H_2O_2 , followed by oxygen transfer to the organic compound.

To clarify the effect of the acidity of p -TsOH on the p -TsOH/HAC system, when using the same molar amounts of HCl or H_2SO_4 to replace p -TsOH, the styrene conversion and selectivity for benzaldehyde were 6% and 89% for HCl, and 9% and 90% for H_2SO_4 , respectively. This suggested that the acidity of the p -TsOH/HAC system was not an important factor for the oxidation of styrene.

Tertiary butanol, a free radical scavenger, was added into the reactant. With only p -TsOH as the catalyst, styrene oxidation gave: in the absence of tertiary butanol, 11% styrene conversion and 82% selectivity for benzaldehyde, and in the presence of tertiary butanol, 13% styrene conversion and 87% se-

Scheme 1. Oxidation of styrene in the *p*-TsOH/HAC/H₂O₂ system.

lectivity for benzaldehyde. The oxidation of styrene was not affected by the radical scavenger, implying that the reaction is a non-radical process. Thus, styrene oxidation with only *p*-TsOH is possible due to the in situ formation of peroxysulfonic acid as a powerful oxidizing reagent [12,16], which reacts with styrene to give the intermediate epoxystyrene. Finally, the oxidation of epoxystyrene yields benzaldehyde.

With both *p*-TsOH and HAC as catalyst, the oxidation reaction gave: in the absence of tertiary butanol, 52% styrene conversion and 75% selectivity for benzaldehyde, and in the presence of tertiary butanol, 43% styrene conversion and 72% selectivity for benzaldehyde. The oxidation of styrene was slightly influenced by the radical scavenger. This implied that the addition of HAC into the *p*-TsOH/H₂O₂ system promoted the formation of peroxysulfonic acid and accelerated the oxidation of epoxystyrene to benzaldehyde (Scheme 1).

4. Conclusions

Either *p*-TsOH with –SO₃H groups or HAC with large amounts of oxygen-containing groups can activate H₂O₂ to oxidize styrene to benzaldehyde. The –SO₃H groups were more effective than the oxygen-containing groups. However, both these two samples showed very low activity for styrene oxidation. There was a strong promotion effect by HAC on the *p*-TsOH/H₂O₂ system. With the simultaneous use of *p*-TsOH and HAC, the styrene conversion increased to eight times higher than that using either *p*-TsOH or HAC, while the selectivity for benzaldehyde only showed a modest decrease. The promotion mechanism of HAC to the *p*-TsOH/H₂O₂ system was attributed to the interaction of the radical reaction (HAC/H₂O₂) and non-radical process (*p*-TsOH/H₂O₂).

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Graphical Abstract

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

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In the *p*-toluenesulfonic acid/activated carbon/H₂O₂ system, there is an interaction of a radical reaction (HAC/H₂O₂) and non-radical process (*p*-TsOH/H₂O₂) for the oxidation of styrene to benzaldehyde.

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对甲苯磺酸/活性炭/双氧水体系选择氧化苯乙烯生成苯甲醛

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摘要: 以双氧水为氧化剂, 研究了对甲苯磺酸和活性炭体系选择氧化苯乙烯生成苯甲醛反应性能。考察了反应时间、温度、催化剂用量、苯乙烯和双氧水摩尔比等对苯乙烯选择氧化性能的影响。结果表明, 对甲苯磺酸和活性炭的用量和用量比是一个重要因素, 但对甲苯磺酸的酸性对氧化反应活性影响不大。对甲苯磺酸和双氧水相互作用, 经非自由基过程氧化苯乙烯。通过分解双氧水产生氢氧自由基, 活性炭显著提高对甲苯磺酸和双氧水体系氧化苯乙烯活性。在惰性或还原气氛中高温处理活性炭能降低其表面含氧基团数量, 增加碱性, 有效分解双氧水, 产生相对较多的OH自由基。与未处理的活性炭相比, 高温处理的活性炭进一步提高了对甲苯磺酸和双氧水体系氧化苯乙烯活性, 但降低了苯甲醛选择性。经磺化, 在活性炭表面引入的 $-\text{SO}_3\text{H}$ 基团比含氧基团($-\text{OH}$, $-\text{COOH}$)更有效与双氧水作用氧化苯乙烯。

关键词: 苯乙烯; 双氧水; 对甲苯磺酸; 活性炭; 氧化

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