

Benzaldehyde synthesis via styrene oxidation by O₂ over TiO₂ and TiO₂/SiO₂

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Abstract

Styrene was oxidized by molecular oxygen over TiO₂ and TiO₂/SiO₂ for the formation of benzaldehyde. In the absence of catalyst at 100 °C and 10 atm O₂, polystyrene is the major product. Over the catalysts, the oxidation of styrene is enhanced with benzaldehyde and formaldehyde being the major whereas phenylacetaldehyde, acetophenone, styrene oxide, benzoic acid, and polymer being the minor products. The polymerization of styrene was initiated by the radicals formed in the oxidation reaction. The addition of radical inhibitor nitrobenzene and/or the employment of a catalyst of high specific surface area can promote the termination of the radicals, and hence improve the selectivity of benzaldehyde.

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1. Introduction

The oxidative conversion of olefins to aldehydes and ketones is important in chemical industry. The current practices can be divided into three categories: (i) the cleavage of C=C bond over materials such as osmium tetroxide and ruthenium tetroxide in stoichiometric amount [1–3], (ii) the ozonolysis of olefins to ozonides and the subsequent conversion to aldehydes or ketones in reductive workup conditions [3,4], and (iii) the oxidation of olefins by hydrogen peroxide [5,6]. Due to waste problem and chemical cost, the practice of using metal oxides and metal salts as oxidants is not desirable [7]. From the viewpoint of environmental protection, oxidation by means of hydrogen peroxide appears to be a better alternative [5,6] in which methyltrioxorhenium [8], nanosized spinel-type Mg_xFe_{3-x}O₄ [9], peroxy vanadium [10], and TS-1 [11] have been reported to be active catalysts. Compared to O₃ and H₂O₂, O₂ is less expensive. For the use of O₂ for olefins oxidation to aldehydes or ketones [12], a reductant such as

aldehyde [13], thiophenol [12], or β-ketoester [14,15] is required, and Cu₂(OH)PO₄ [16] and CoCl₂ [17] were found to be catalytically active. The reported processes, however, are slow. In this article, we report the use of TiO₂ and TiO₂/SiO₂ as catalyst for the oxidative conversion of styrene to benzaldehyde using O₂ as oxidant.

2. Experimental

2.1. Catalyst preparation

For the generation of SiO₂, 2.116 g of tetraethyl orthosilicate (Aldrich) was added to a solution of poly ethylene glycol-ran-propylene glycol (0.500 g; average M_n ca. 12,000, Aldrich) in ethanol (20.0 mL). The mixture was stirred and left (three days) in ambient environment for gelation. The gel was then kept at 50 °C (in water bath) for one day and at 120 °C for 4 h to obtain a dry bulk sample, which was calcined at 450 °C for 5 h to give SiO₂.

For the preparation of TiO₂, 1.000 g of poly ethylene glycol-ran-propylene glycol and 3.460 g of TiCl₄ were mixed with 40.0 mL of ethanol to obtain a solution. The solution was left for gelation in ambient environment for

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three days. The resulted gel was kept at 50 °C for one day and at 120 °C for 4 h for the generation of a dry bulk sample, which was calcined at 450 °C for 5 h to give TiO₂.

The TiO₂/SiO₂ (1/1) catalyst was prepared by the following method: 0.500 g of poly ethylene glycol-ran-propylene glycol and 1.730 g of TiCl₄ were dissolved in 20.0 mL of ethanol to obtain a solution denoted as A, and 0.500 g of poly ethylene glycol-ran-propylene glycol and 2.116 g of tetraethyl orthosilicate (Aldrich) were dissolved in 20.0 mL of ethanol to obtain a solution denoted as B. A solution denoted as C was obtained by mixing 10.0 mL of solution A and 10.0 mL of solution B. The solution C was left for gelation for three days in ambient environment, kept at 50 °C in a water bath for one day and at 120 °C for 4 h. The resulted bulk sample was calcined at 450 °C for 5 h to give the catalyst.

2.2. Reaction and analysis

In a typical run, the catalyst and styrene were charged into a 1.5 mL autoclave, which was connected to an oxygen source of 10.0 atm. The reaction was carried out at a desired temperature for 4 h. After the reaction period, the reactor was cooled to room temperature (RT), and then isolated from the oxygen line for products collection. The collected samples were analyzed on a GC (Agilent 6890N) with TCD and a GC/MS (Agilent 6890N/

5973N). The GC and GC/MS signals were calibrated against those of standard samples. The polymer products cannot be analyzed by the GC and GC/MS techniques. We take the unaccountable amount of styrene in the experiment being the portion consumed in polymer formation.

2.3. XRD measurement

The XRD measurements were conducted over a Philips PW3040/60 X-ray diffraction spectrometer with CuK α radiation.

3. Results

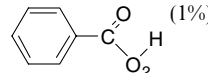
In the oxidation of styrene (4 h in O₂ of 10 atm), benzaldehyde, formaldehyde, acetophenone, phenyl-acetaldehyde, styrene oxide, and polystyrene are found in the liquid phase, whereas CO and formaldehyde in the gas phase. In the absence of catalyst, there is the formation of benzaldehyde but over half of the consumed styrene is converted to polystyrene; at 110 °C, styrene conversion is 99.2% but benzaldehyde selectivity is only 27.5% (Table 1). The presence of SiO₂ (502.8 m²/g) at 100 °C does little to the conversion of styrene but enhances the benzaldehyde selectivity (from 48.7% in the absence of catalyst to 86.3%). Over the TiO₂ (31.4 m²/g) catalyst, styrene conversion is

Table 1
Specific surface area and performance of catalysts in styrene oxidation

Catalyst	<i>t</i> (h)	<i>S</i> (m ² /g)	<i>T</i> (°C)	<i>X</i> (%)	<i>Y</i> (%)	Selectivity (%)					
						<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
No	4		100	19.5	0.05	48.7	0	0	0	0	51.3
No	4		110	99.2	0.01	27.5	1.5	2.5	0.3	0.6	67.6
SiO ₂	4	502.8	100	21.8	0.04	86.3	0	0	0	0	13.7
TiO ₂	4	31.4	100	70.2	0.02	40.7	3.9	3.4	0.5	0.1	51.4
TiO ₂ (P ₂₅)	4	50.1	100	98.2	0.01	50.1	1.9	6.5	3.86	3.1	34.6
TiO ₂ /SiO ₂	1	470.3	100	0	0	0	0	0	0	0	0
TiO ₂ /SiO ₂	2	470.3	100	36.0	0.06	100	0	0	0	0	0
TiO ₂ /SiO ₂	4	470.3	100	70.9	0.01	75.3	7.90	1.2	1.2	0	14.4
TiO ₂ /SiO ₂	6	470.3	100	99.5	0.01	43.4	15.4	5.8	8.7	4.3	22.3

Notes: Reactions were carried out at a styrene to *M* (*M* denotes the total number of moles of Ti and Si in the catalyst, and the mass of styrene employed was 0.720 g) molar ratio of 14:1. (*t*: reaction time, *S*: specific surface area of catalyst, *T*: reaction temperature, *X*: styrene conversion, *Y*: the molar ratio of formaldehyde to benzaldehyde, *A*: benzaldehyde selectivity, *B*: phenylacetaldehyde selectivity, *C*: acetophenone selectivity, *D*: styrene oxide selectivity, *E*: benzoic acid selectivity, *F*: selectivity of polymer.). P₂₅ refer to the commercial TiO₂ P₂₅. (Degussa 50.1 m²/g).

Table 2
Effect of radical initiator (1 mol%) on styrene oxidation (4 h at 100 °C) over TiO₂/SiO₂

Reagent (% in styrene)	<i>T</i> (°C)	<i>X</i> (%)	<i>Y</i>	Selectivity (%)			
				<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>
HNO ₃ (1%)	100	99.8	0.23	2.8	0.1	0.2	98.8
H ₂ O ₂ (1%)	100	99.3	0.71	1.4	0.1	0.1	98.4
 (1%)	100	99.8	0.09	3.60	0.30	0.3	95.8

Notes: Reaction parameters are the same as those of Table 1. *X* denotes styrene conversion; *Y* denotes the molar ratio of formaldehyde to benzaldehyde; *A* denotes benzaldehyde selectivity; *B* denotes phenylacetaldehyde selectivity; *C* denotes acetophenone selectivity; and *D* denotes selectivity of polymer.

Table 3
Effect of nitrobenzene addition (5 mol%) on styrene oxidation (4 h at 100 °C) over SiO₂, TiO₂, and TiO₂/SiO₂

Catalyst	T (°C)	X (%)	Y (%)	N (M)	Selectivity (%)					
					A	B	C	D	E	F
SiO ₂	100	1.1	0.24	5.0	100	0	0	0	0	0
TiO ₂	100	75.5	0.02	5.0	72.2	3.8	4.5	1.8	0	18.7
TiO ₂ /SiO ₂	100	51.7	0.01	5.0	93.5	3.7	1.7	0.2	0	0.8

Note: Reaction parameters are the same as those of Table 1. X denotes styrene conversion; Y denotes the molar ratio of formaldehyde to benzaldehyde; A denotes benzaldehyde selectivity; B denotes phenylacetaldehyde selectivity; C denotes acetophenone selectivity; D denotes styrene oxide selectivity; E denotes benzoic acid selectivity; and F denotes selectivity of polymer.

enhanced (from 19.5% in the absence of catalyst to 70.2%), but benzaldehyde selectivity (40.7%) was low because of enhanced polymerization. Over commercial TiO₂ (P₂₅ from Degussa, 50.1 m²/g), benzaldehyde selectivity is 50.1% and styrene conversion is 98.2%, higher than that observed over the TiO₂ sample prepared by us. Over the TiO₂/SiO₂ catalyst at 100 °C, there is no reactivity detected within the first hour. After 2 h, styrene conversion is 36.0% and benzaldehyde and formaldehyde are the observed products in the liquid phase (formaldehyde and CO are also detected as gaseous products). In this study, only products with benzene ring are considered in the calculation of selectivity. After 4 h, besides benzaldehyde, formaldehyde and CO, phenylacetaldehyde, acetophenone, styrene oxide, and polymer are formed. The results indicate that formaldehyde and benzaldehyde are primary, whereas phenylacetaldehyde, acetophenone, styrene oxide, and polymer are secondary products. Compared to SiO₂, TiO₂, and TiO₂ (P₂₅), the TiO₂/SiO₂ catalyst gives the best yield of benzaldehyde after 4 h of reaction at 100 °C. After 6 h of reaction over the TiO₂/SiO₂ catalyst, there is a decline in benzaldehyde yield due to the enhanced formation of side-products. Referring to Table 1, the selectivity of benzaldehyde des-

cends in the order of: SiO₂ (86.3%) > TiO₂/SiO₂ (75.3%) > TiO₂ (P₂₅) (50.1%) > TiO₂ (40.7%), whereas the specific surface area (in m²/g) declines in the order of: SiO₂ (502.8) > TiO₂/SiO₂ (470.3) > TiO₂ (P₂₅) (50.1) > TiO₂ (31.4). There appears to be a correlation between specific surface area and benzaldehyde selectivity: the bigger the specific surface area, the higher is the benzaldehyde selectivity. Despite the effect of specific surface area on the overall catalytic activity is still uncertain, one can address the trend of benzaldehyde selectivity based on the concept of “radical termination” on the surface of the catalysts as discussed later in this article.

In the oxidation of styrene in the absence of catalyst, polymerization of styrene is major. To investigate if the polymerization were initiated by radicals, the addition of an oxidative radical initiator would lead to more polymer formation. It is known that there is the generation of NO, NO₂, and N₂O radicals in HNO₃ decomposition at elevated temperature. As shown in Table 2, the addition of HNO₃ led to high polymer selectivity. The addition of oxidative radical initiators, such as hydrogen peroxide and perbenzoic acid also led to high polymer generation. It is clear that in the oxidation of styrene, benzaldehyde generation is not a result of styrene interaction with oxidative radicals. When 5 mol% of nitrobenzene (a radical inhibitor known to retard styrene polymerization [18]) was added into the reaction system, there was significant

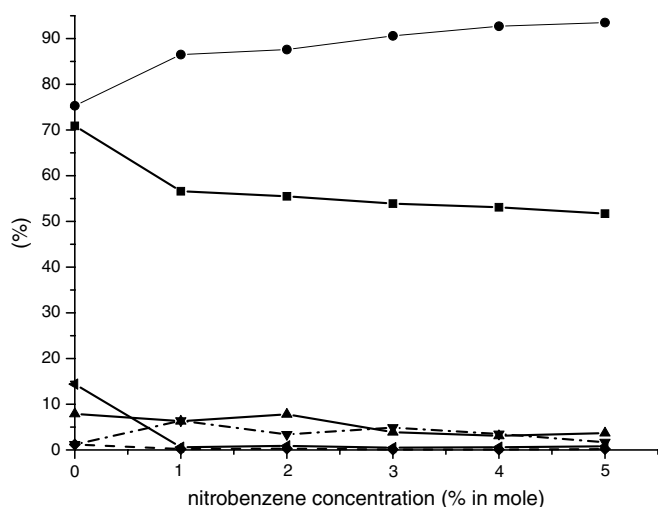


Fig. 1. The influence of nitrobenzene concentration on catalytic performance over TiO₂/SiO₂ at 100 °C in 4-h of styrene oxidation: styrene conversion (■), benzaldehyde selectivity (●), phenylacetaldehyde selectivity (▲), acetophenone selectivity (▼), styrene oxide selectivity (◆), and polymer selectivity (◄).

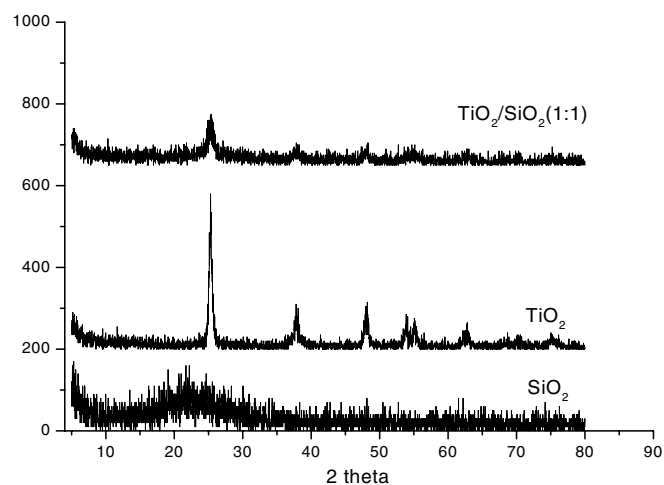


Fig. 2. The XRD patterns of SiO₂, TiO₂, and TiO₂/SiO₂.

enhancement in benzaldehyde selectivity (Table 3). The correlation between nitrobenzene concentration and the selectivity of products is shown in Fig. 1. Even at nitrobenzene concentration as low as 1.0%, the retardation of styrene polymerization was significant, and with the increase in nitrobenzene concentration, there was a gradual increase in benzaldehyde selectivity.

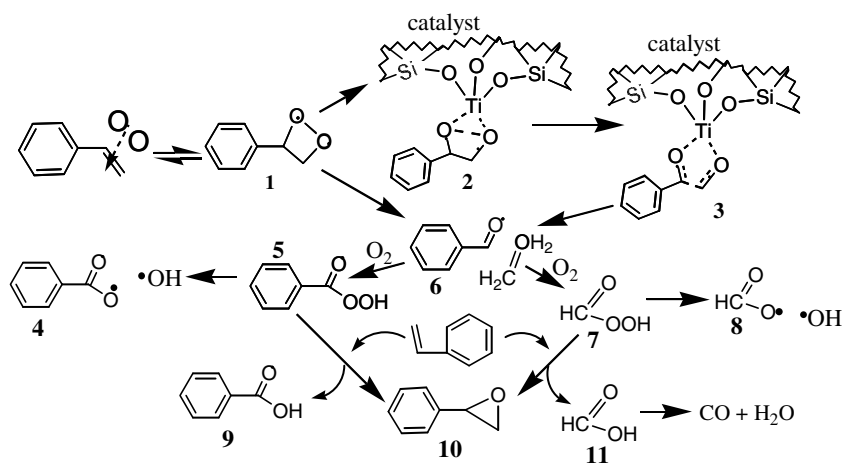
The XRD patterns of the catalysts are shown in Fig. 2. The silica material is amorphous and TiO_2 is anatase. The XRD pattern of $\text{TiO}_2/\text{SiO}_2$ (1:1) just shows weak signals of anatase. Compared to the TiO_2 sample, the TiO_2 in the $\text{TiO}_2/\text{SiO}_2$ catalyst is poor in crystallinity and should be high in dispersion.

4. Discussion

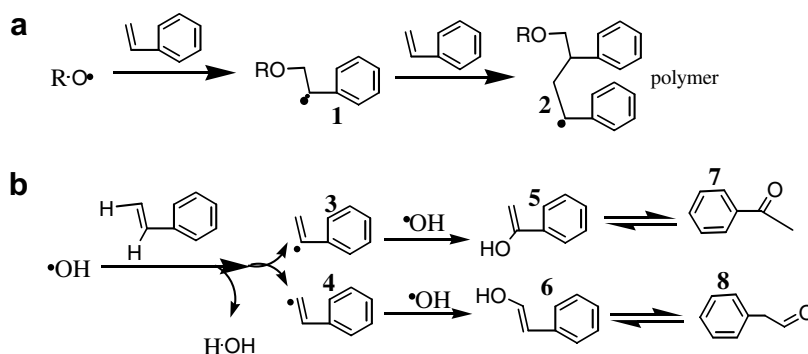
The dispersing of TiO_2 in SiO_2 might lead to a situation where Ti^{4+} ions are coordinated to $-\text{O}-\text{Si}$ entities. If Ti^{4+} ions of this kind were present on the surface of the catalyst, they could play an important role in the oxidation of styrene. In the oxidation of olefins to olefin oxides using hydrogen peroxide as oxidant, Ti^{4+} ions of this kind are known to be catalytically active [19]. The role of Ti^{4+} ions is to activate the neighboring peroxide ligands by with-

drawing the electron cloud and reducing the electron density of the oxygen atoms. Despite the interaction between Ti^{4+} ions and intermediates in styrene oxidation by O_2 could be different from that in olefin epoxidation by hydrogen peroxide, we consider that it is possible to have Ti^{4+} interaction with peroxide ligands on the surface of the $\text{TiO}_2/\text{SiO}_2$ catalyst during the oxidation of styrene by O_2 . Based on what have been discussed so far, we propose reaction pathways for the formation of benzaldehyde and the by-products (Schemes 1 and 2).

The first step is a non-catalytic auto-oxidation, which forms peroxide **1** (Scheme 1), and the peroxide intermediate decomposes directly to benzaldehyde **6** and formaldehyde. In the presence of TiO_2 or $\text{TiO}_2/\text{SiO}_2$, peroxide **1** converts to benzaldehyde and formaldehyde readily. We suggest that it is peroxide **1** that interacts with the Ti^{4+} sites to form intermediates **2** and **3** in which the cracking of $\text{O}-\text{O}$ and $\text{C}-\text{C}$ bonds is promoted. It is known that aldehydes react with oxygen molecules to form peracids. In the current cases, the peracids are perbenzoic acid **5** and performic acid **7**. Since the molar ratios of formaldehyde to benzaldehyde are far below 1:1 (Tables 1 and 3), we believe that it is performic acid **7** that is oxidized to CO in a significant manner. On the other hand, the concentration of perben-



Scheme 1.



Scheme 2.

zoic acid should not be high because the amount of benzoic acid among the products is not significant. The peracids **5** and **7** react with styrene to form olefin oxide **10**. The peracids can also decompose to $\cdot\text{OH}$ and the corresponding oxidative radicals **4**, and **8** [20]. These oxidative radicals can initiate the polymerization of styrene to form polymers via intermediates **1** and **2** as shown in Scheme 2a. In addition, the $\cdot\text{OH}$ radicals can react with styrene to form acetophenone **7** via intermediates **3** and **5** whereas phenylacetaldehyde **8** can be produced via intermediates **4** and **6** as shown in Scheme 2b.

The suggested reaction pathways are consistent with the results of this study. Since that at 110 °C in the absence of catalyst, benzaldehyde, formaldehyde, polymer, styrene oxide, phenylacetaldehyde, and acetophenone are detected products (Table 1). The results of Table 2 indicate that the addition of radical initiators HNO_3 , H_2O_2 , and perbenzoic acid enhances styrene polymerization. The results of Table 3 show that the addition of the radical inhibitor nitrobenzene brings about the improvement in benzaldehyde selectivity. The overall results of Tables 2 and 3 confirm that the polymerization of styrene is initiated by oxidative radicals. As depicted in Table 1, styrene conversion at 100 °C over SiO_2 (21.8%) is close to that in catalyst absence (19.5%), but benzaldehyde selectivity of the former (86.3%) is much higher than that of the latter (48.7%). Also, the results of Table 1 show that a catalyst of bigger specific surface area gives higher benzaldehyde selectivity. The phenomenon can be explained by the related steps involving radicals because a catalyst of bigger specific surface area would certainly mean a bigger chance of having the radicals terminated.

On the other hand, the reaction pathways of Schemes 1 and 2 suggest that benzaldehyde and formaldehyde are primary products, whereas phenylacetaldehyde, acetophenone, styrene oxide, benzoic acid, and polymers are products of multi-step reactions. The results of Table 1 demonstrate that over the $\text{TiO}_2/\text{SiO}_2$ catalyst, benzaldehyde, formaldehyde, and CO are produced within the first 2 h of reaction whereas phenylacetaldehyde, acetophenone, styrene oxide, benzoic acid, and polymers are formed in 4 h of reaction. Hence, the reaction pathways of Schemes 1 and 2 are consistent with the experimental results.

In conclusion, styrene can be oxidized to benzaldehyde by O_2 and styrene polymerization can be a major side-reaction. At 100 °C and 10 atm O_2 pressure, benzaldehyde and polymer generation occurs even without the help of a cat-

alyst. The presence of TiO_2 and $\text{TiO}_2/\text{SiO}_2$ catalysts, nevertheless, promotes the yield of benzaldehyde. Reaction schemes consistent with the experimental results have been proposed. The polymerization of styrene is initiated by oxygen-containing radicals formed in the oxidation of styrene. The termination of the radicals by nitrobenzene and catalysts of big specific surface area results in the retardation of the polymerization steps and hence improve the selectivity of benzaldehyde.

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