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Reaction-Controlled Phase Transfer Catalysis for Styrene Epoxidation to Styrene Oxide with Aqueous Hydrogen Peroxide

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Abstract:

The epoxidation of styrene catalyzed by a reaction-controlled phase transfer catalyst $[(C_{18}H_{37}\,(30\%)+C_{16}H_{33}(70\%))N(CH_3)_3]_3$-$[PW_4O_{16}]$ with H_2O_2 in a biphasic medium was investigated. Under certain conditions, the selectivity for styrene oxide was 95%, the conversion of styrene based on H_2O_2 was 85%, and the reaction time was less than 1 h. During the reaction, this catalyst powder formed soluble active species by the action of H_2O_2, was recovered as a precipitate, and was reused after H_2O_2 was used up. After two times recycling, the catalyst kept almost the same activity.

1. Introduction

Styrene oxide is one of the most important fine chemical intermediates for producing perfume, drugs, sweeteners, epoxy resins, etc. Current commercial production usually employs the bromohydrin method, which gives rise to serious problems of equipment corrosion and environmental pollution. Thus, environmental friendly catalytic methods for epoxidation with clean oxidant are actively investigated. Aside from oxygen, aqueous hydrogen peroxide is probably the terminal oxidant because it is inexpensive, relatively safe and easy to handle, and produces water as the sole coproduct.

With aqueous hydrogen peroxide as oxidant, several systems have been reported over the last two decades. The heterogeneous catalysts including Ti/SiO_2,[1] TS-1,[2] mixed metal oxide,[3] hydroxyapatites,[4] and hydrotalcites,[5] etc. have been reported, and some good results were obtained. However, these technologies have been not applied in production.

Homogeneous catalytic epoxidation of styrene can take place under mild conditions and gives a good selectivity with porphyrins,[6] or "soluble metal oxides" such as methyltrioxorheniun[7] ($MeReO_3$ or MTO) and the Venturello−Ishii catalytic system.[8] However, there is a problem common in these catalytic systems: the difficulty of catalyst separation and reuse.

Recently, we reported a new catalytic system: reaction-controlled phase transfer catalysis.[9] This catalytic system solves the recycling problem of homogeneous catalysts. In this way, the catalyst can be recovered and used again. In the present work, we synthesized a cheaper "reaction-controlled phase transfer catalyst" with a practical method and applied it to epoxidation of styrene to styrene oxide.

2. Experimental Section

2.1. Preparation of Catalyst. The catalyst was prepared by the same procedure reported previously.[10] A suspension of tungstic acid (2.50 g, 10 mmol) in 10 mL of 30% aqueous H_2O_2 was heated to 60 °C and stirred for 1 h. To the obtained colorless solution, 85% H_3PO_4 (0.29 g, 2.5 mmol) was added at room temperature and then stirred for half an hour. To the resultant solution, $(C_{18}H_{37}\,(30\%) + C_{16}H_{33}\,(70\%))N^+$ $(CH_3)_3Cl$ (3.51 g, 7.5 mmol) in 1,2-dichloroethane (40 mL) was added dropwise with stirring. Stirring was continued for an additional 1 h. Then the catalyst was precipitated. The catalyst was washed by deionized water and dried under infrared light.

2.2. Characterization of Catalyst. The catalyst prepared was characterized by ^{31}P MAS NMR, FT-IR, and ICP. The ^{31}P MAS NMR spectroscopy of solid catalyst with high-power proton decoupling was performed at 161.9 MHz with a BBO MAS probe head using 4-mm ZrO_2 rotors, 2.0-s pulses, and 2-s repetition times; 2048 scans were made with samples spun at 8 kHz and referenced to 85% H_3PO_4. FT-IR spectra were recorded on a NEXUS 470 FT-IR spectrometer. ICP was performed on Atom Scan Advantage spectrometer.

2.3. Reaction Procedure for Styrene Epoxidation. Into a 30-mL flask were added styrene (0.83 g, 8 mmol), 10 mL of mixed solvent of toluene and TBP (tributyl phosphate), 50% H_2O_2 (0.18 g, 2.6 mmol), and the catalyst (0.0256 g, 0.013 mmol). The reaction was maintained at 65 °C for some time with vigorous stirring. After the reaction, the reaction mixture was cooled to room temperature. The organic phase

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***Table 1.* Solvent screening for styrene epoxidation**[a]

solvent	conversion (%)[b]	selectivity (%)		recovery efficiency (wt %)
		epoxide	benzaldehyde	
$C_2H_4Cl_2$	>99	76.1	13.1	0
acetone[c]	73.6	7.4	2.8	*d*
acetonitrile	>99	43.1	21.8	10
toluene	100	40.5	13.2	91.4
toluene:TBP (1:1)	92.9	83.7	5.1	35.2

[a] Reaction conditions: 0.83 g (8 mmol) styrene, styrene:H_2O_2:cat = 600: 200:1(mol), 10 mL solvent, 65 °C. [b] Conversion was based on H_2O_2. [c] Temperature = 48 °C. [d] Catalyst is insoluble over the reactive time.

was analyzed by a GC equipped with a flame ionization detector and a packed column containing SE-30 as the stationary phase for detecting product using the internal standard method.

3. Results and Discussion

3.1. Characterization of Catalyst Structure. The catalyst structure has been reported in our former study.[10] By ^{31}P MAS NMR spectroscopy and ICP analysis, the catalyst is a mixture. The mixture consists of several heteropolyphosphatotungstates exhibiting peaks at 5.2, −0.8, −13.5, and −26.1 ppm, respectively. Element analysis by ICP shows that the W/P ratio of catalyst is 4.8. IR spectrum of the catalyst shows no peroxo band.

3.2. Effect of Solvent. Since the catalyst used has a dissolving−precipitating phenomenon during the reaction, suitable solvent must be selected to ensure the catalyst will dissolve in a reaction system in the presence of H_2O_2 and precipitate from the reaction system with the H_2O_2 being used up. For an epoxidation reaction with aqueous hydrogen peroxide, a solvent should preferably be polar, nonbasic, and inert under the oxidizing conditions. Several classes of solvent were screened first (Table 1). $C_2H_4Cl_2$ was not suitable for this epoxidation because the catalyst is very soluble so that it cannot precipitate from the reaction system after the completion of reaction. When using acetone as solvent, the catalyst could not dissolve into the solvent and gave a very poor yield for styrene oxide, probably due to styrene polymer. Acetonitrile, owing to its strong polar and coordination capacity, probably took part in the epoxidation and gave a higher selectivity for benzaldehyde (byproduct) as well as a very poor recovery efficiency of the catalyst. When using toluene as solvent, the reaction proceeded quickly and had a very good phenomenon of dissolving and precipitating, but the selectivity for styrene oxide was not good. Considering that the catalyst used is composed of two parts (one is an inorganic anion, which has good solubility in polar solvent, the other is organic with a long chain, which has good solubility in nonpolar solvent), we should adopt a solvent composed of a mixture of polar and nonpolar (or weakly polar) solvents to perform the epoxidation. So then we selected a solvent mixture of toluene and TBP (tributyl phosphate). As can be seen from Table 1, the equally mixed solvent of toluene and TBP showed a profound effect on the product distribution. When using toluene and TBP (1:1) instead of toluene alone as solvent, the selectivity for styrene oxide increased from 40.5 to 83.7%, and the selectivity for benzaldehyde decreased from13.2 to 5.1%; however, the recovery efficiency of the catalyst was still low. For optimizing solvent composition, we examined the effect of the ratio of toluene to TBP on the epoxidation, and the results are listed in Table 2. The results show that TBP has a very good effect on the selectivity for styrene oxide and the recovery efficiency of catalyst. The results for epoxidation and the recovery efficiency of catalyst are better when the ratio of toluene to TBP is 2:3 or 3:2.

***Table 2.* Effect of toluene to TBP ratio (v/v) on styrene epoxidation**[a]

toluene (mL)	TBP (mL)	conversion (%)	selectivity (%)		recovery efficiency (wt %)
			epoxide	benzaldehyde	
8	2	79.3	76.4	15.4	78.5
6	4	95.2	88.0	5.2	88.7
4	6	90.7	88.4	5.0	81.6
2	8	74.8	85.4	4.2	

[a] Reaction conditions were the same as those for Table 1.

***Table 3.* Effect of styrene to H_2O_2 molar ratio on the epoxidation of styrene**[a]

styrene/H_2O_2	conversion[b] (%)	selectivity(%)		recovery efficiency (wt %)
		epoxide	benzaldehyde	
1	60.2	20.6	28.5	28.1
2	83.3	85.2	7.8	85.5
3	90.7	88.4	5.0	81.6

[a] Reaction conditions: 0.83 g (8 mmol) styrene, 0.0256 g catalyst, 65 C; 10 mL mixed solvent toluene (4 mL) + TBP (6 mL). [b] Conversion was based on H_2O_2.

3.3. Effect of Styrene-to-H_2O_2 Molar Ratio. Table 3 gives the results of epoxidation with the different molar ratios of styrene to H_2O_2. As expected, the conversion of styrene increased from 60.2 to 90.7% with the styrene-to-H_2O_2 molar ratio increasing from 1 to 3, mainly due to H_2O_2 utilization increasing for styrene oxidation. The selectivity for styrene oxide also increased from 20.6 to 88.4%, and the selectivity for benzaldehyde decreased from 28.5 to 5.0%. It seems that benzaldehyde is formed mainly via the further oxidation of the epoxide. Moreover, it also showed that styrene oxide can be transferred to benzaldehyde when using styrene oxide instead of styrene as the starting material under the same catalytic epoxidation conditions. The recovery efficiency of catalyst also increased from 28.1 to 85.5% with the increase in the styrene/H_2O_2 molar ratio from 1 to 2, and when the ratio is 3, the catalyst had almost the same recovery efficiency with styrene/H_2O_2 = 2.

3.4. Effect of Temperature. The reaction was studied at four different temperatures in the range of 65−95 °C (Table 4). As expected, with rising reaction temperature, the reaction rate was raised significantly. When the temperature was increased from 65 to 85 °C, the reaction time decreased from 4.5 h to 40 min, and the styrene conversion, product distribution, and catalyst recovery efficiency almost did not

Table 4. **Effect of temperature on styrene epoxidation**[a]

T (°C)	time (h)	conversion[b] (%)	selectivity (%) epoxide	selectivity (%) benzaldehyde	recovery efficiency (wt %)
65	4.5	90.7	88.4	5.0	81.6
75	3	93.3	86.3	5.0	85.5
85	1.25	96.5	89.3	7.5	82.4
95	0.5	99.0	77.3	7.2	64.1

[a] Reaction conditions: styrene 0.83 g; styrene:H_2O_2:cat = 600:200:1; solvent, toluene (4 mL) + TBP (6 mL). [b] Conversion was based on H_2O_2.

Table 5. **Effect of the concentration of inhibitor onstyrene epoxidation**[a]

inhibitor (g)	conversion[b] (%)	selectivity (%) epoxide	selectivity (%) benzaldehyde	recovery efficiency (wt %)
0.0035	102.0	84.5	1.9	93.0
0.0175	91.3	90.7	2.5	90.0
0.0280	85.1	96.9	2.2	94.1

[a] Reaction conditions: styrene, 0.83 g; styrene:H_2O_2:cat = 600:200:1, reaction time, 50 min; temperature, 85 °C, solvent, toluene (6 mL) + TBP (4 mL). [b] Conversion was based on H_2O_2.

change. However, at 95 °C, the selectivity for styrene oxide decreased to 77.3% probably due to the slight polymerization of styrene monomer as well as the decomposition of hydrogen peroxide.

3.5. Catalyst Recycle. To inhibit the slight polymerization of styrene, we added an inhibitor (2,6-di-*tert*-butyl-*p*-cresol) into the reaction system to perform the catalytic recycle. Table 5 lists the effect of changing the quantity of the inhibitor on styrene epoxidation. With the increase of the quantity of inhibitor from 0.0035 to 0.0280 g, the styrene conversion decreased from 102.0 to 85.1% along with an increase in selectivity for styrene oxide from 84.5 to 96.9%. This indicates that when employing 0.0280 g of inhibitor, the polymerization of styrene can be effectively inhibited.

Under these conditions, the catalyst recycle was performed. The results of the recycling of the catalyst are listed in Table 6. For the fresh catalyst, the conversion of styrene was 85.1%, and the selectivity for styrene oxide was 96.9%. At the end of the reaction, the recovery efficiency of the catalyst was about 94 wt %. In the subsequent runs using the mixture of the recycled catalyst and a little fresh catalyst (for making the quantity of the second run catalyst the same as the first run one), the conversions of styrene were 83.2% and 86.9%, respectively, and the selectivity for styrene oxide was about 96%. The catalyst showed a stable activity in the recycles.

Table 6. **The results of the recycle of the catalyst**[a]

cat.	conversion[b] (%)	selectivity%) epoxide	selectivity%) benzaldehyde	recovery efficiency (wt %)
fresh	85.1	96.9	2.2	94.1
cycle1	83.2	94.8	2.3	93.8
cycle2	86.9	97.1	2.0	91.8

[a] Reaction conditions: inhibitor, 0.0285 g; other conditions were the same as those of Table 5. [b] Conversion was based on H_2O_2.

The reaction was carried out in a larger scale (10 times), the conversion of styrene was 82.0%, and the selectivity for styrene oxide was 96.6%. The recovery efficiency of the actalyst was 89.2%.

4. Conclusions

Styrene epoxidation to styrene oxide with high selectivity (>95%) and conversion (85%) can be achieved using the clean oxidant of hydrogen peroxide in a chloride-free/aqueous biphasic system under the reaction-controlled phase transfer catalyst The catalyst can be separated easily from the reaction mixture and has almost stable catalytic activity. It is expected that it can be used in other substrate epoxidations.

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