Propene Epoxidation with In-Site H_2O_2 Produced by H_2/O_2 Non-Equilibrium Plasma

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A novel in-site H_2O_2 strategy is proposed for the liquid-phase epoxidation of propene catalyzed by titanium silicalite (TS-1). Said in-site H_2O_2 strategy is based on the direct synthesis of H_2O_2 from H_2 and O_2 under atmospheric pressure via nonequilibrium plasma reactions. Methanol is used to absorb H_2O_2 from the dielectric barrier discharge (DBD) reactor. Methanol also serves as the desired solvent for the liquid-phase epoxidation reactor. The efficiency of the integrated process for in-site synthesis of H_2O_2 reached 69% selectivity, and 62% yield with a nonexplosive H_2/O_2 mixture when the DBD reactor worked at an input power of 3.5 W (energy consumption 12.4 kWh/kg H_2O_2). The liquid-phase epoxidation of propene using the in-site H_2O_2 successfully proceeded over an 18 h time course under the conditions of 50 °C and 3.0 MPa, more than 92% H_2O_2 conversion and more than 93% PO selectivity were obtained. The two-reactor integrated process worked smoothly during continuous operation, no performance decay was observed for both the DBD reactor and the epoxidation reactor. These facts mean that our in-site H_2O_2 strategy for PO synthesis is promising. © 2007 American Institute of Chemical Engineers *AIChE J,* 53: 3204–3209, 2007

Keywords: in-site H_2O_2, H_2 and O_2, nonequilibrium plasma, propene oxide, TS-1

Introduction

Propene oxide (PO) is one of the most important starting materials in the chemical industry. It is widely used for making polyurethane, unsaturated resins, surfactants and other products. PO is currently produced by two different types of processes: the chlorohydrin process and the hydroperoxide process. The chlorohydrin process has serious environmental problem due to the use of chlorine (usually excretes more than 40 tons $CaCl_2$-containing wastewater per ton PO). The hydroperoxide processes have troublesome coproduct problems due to the use of ethylbenzene or isobutane as oxygen carriers (produce more than 2 ton styrene or *tert*-butanol per ton PO).[1] Nowadays, because of environmental and economical reasons, new PO-synthesizing process that can get rid of these problems is badly wanted. It is well known that PO can be produced by the epoxidation of propene with dilute hydrogen peroxide (H_2O_2) over titanium silicalite (TS-1) in methanol solvent. This epoxidation process can produce PO with very high-selectivity (ca. more than 95%), and, theoretically, only excretes H_2O as byproduct. It has been extensively studied as an ideal alternative for the commercial PO processes in the last decades.[1–3] However, the commercialization of it has been hindered by the supply of H_2O_2 to a large degree. Currently, H_2O_2 is almost exclusively produced by the anthraquinone process, the production cost, the equipment investment, and the transportation cost of H_2O_2 are too high for the production of bulk chemicals like PO. So far, strategies that have been proposed to cope with the problems of H_2O_2 include: (1) integrate the anthraquinone process for H_2O_2 synthesis with the propene epoxidation process catalyzed by TS-1.[4–7] In such a combined process, suitable solvent system has to be developed to facilitate not only the epoxidation of propene, but also the sequential hydrogenation

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and oxidation of alkyl-anthraquinone; (2) directly synthesize H_2O_2 from H_2/O_2 mixture with supported palladium (or palladium alloys) in acidified solvents (ca. water, methanol).[19–25] The handicaps of this approach in commercialization are the difficulties in obtaining high concentration of H_2O_2 with high-selectivity; (3) *in situ* generate oxidant from H_2 and O_2 over supported gold catalyst, the synthesis of oxidant and the epoxidation of propene all occur in gas-solid phase. This route is known as gas-phase epoxidation,[8,9] and (4) *in situ* generate H_2O_2 from H_2 and O_2 over supported Pd (Pt) catalyst, the synthesis of H_2O_2, and the epoxidation of propene all proceed in liquid-solid phase.[10–12] In the latter two strategies, the increases of the formation selectivity and rate of the *in situ* oxidant are still challengeable.

Articles published in 1960s teach that H_2O_2 can be generated in the gaseous nonequilibrium plasma of H_2/O_2 mixture via free-radical reactions.[13–15] However, the yield of hydrogen peroxide based on oxygen was low (<5%). Most recently, we have developed a new and highly efficient technique for the direct synthesis of H_2O_2 from the reactions of H_2/O_2 nonequilibrium plasma.[16] Depart from this, we herein propose and test a novel in-site H_2O_2 strategy for the TS-1 catalyzed epoxidation of propene.

Experimental

Process outline

The basic idea of our in-site H_2O_2 strategy was to combine the H_2/O_2 nonequilibrium plasma reactions (for the direct synthesis of H_2O_2) with the TS-1 catalyzed epoxidation of propene. As it can be seen in Figure 1, the integrated process for actualizing the new idea consisted of two units: one was a pyrex dielectric barrier discharge (DBD) reactor and its control circuit, the other was a fixed-bed catalytic reactor. The DBD reactor was designed to produce nonequilibrium plasma from a mixture of H_2/O_2, and to generate H_2O_2, thereby. The DBD reactor was prepared according to our previous work,[16] modification was made by using a nonmetal composite high-voltage electrode. The flow rates of H_2 and O_2 feedstocks for the DBD reactor were controlled by mass flow controllers. The circuit setup designed for the DBD reactor is shown in Figure 2. An alternating current power supply was employed to generate high voltage with a frequency of 14 kHz. The values of input voltage and input current were measured by a TDS 3012B Tektronix oscilloscope using a high-voltage (Tektronix 6015A), and a low-voltage probe (Tektronix P3010), respectively. The voltage across a standard resistor (50 Ω) in series with the reactor was used to determine the input current, which could be calculated through the voltage value measured with the low-voltage probe by taking the resistor into account.[17] The input power value was calculated by the oscilloscope with the values of voltage and current. The fixed-bed reactor was a tubular stainless steel reactor with an inner dia. of 7 mm, and a volume of 15.4 ml. It was used to pack TS-1 catalyst and to produce PO thereon. A water-jacket was used to heat the fixed-bed reactor. In these laboratory studies, the recycles of the unreacted H_2 and O_2, as well as methanol solvent were not made. Therefore, three pumps were employed: one for compensating fresh methanol to the H_2O_2 collector; one for outputing H_2O_2-methanol solution to the epoxidation reactor, and one for feeding liquid propene to the epoxidation reactor.

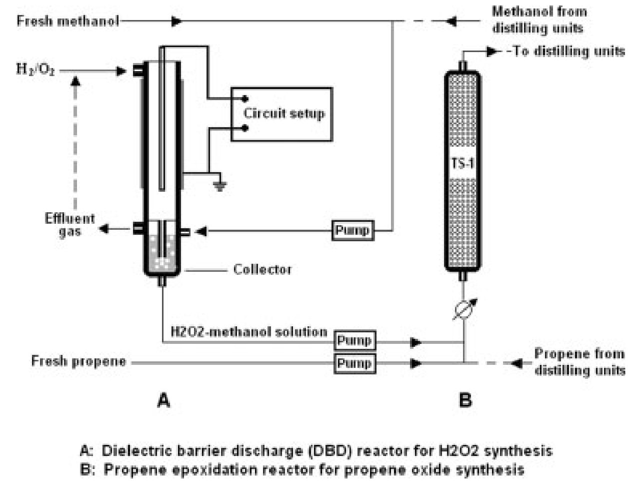

Figure 1. Flow chart of the novel propene oxide synthesizing integration process based on H_2/O_2 nonequilibrium plasma reactions (for in-site H_2O_2 synthesis), and the titanium silicalite (TS-1) catalyzed epoxidation of propene.

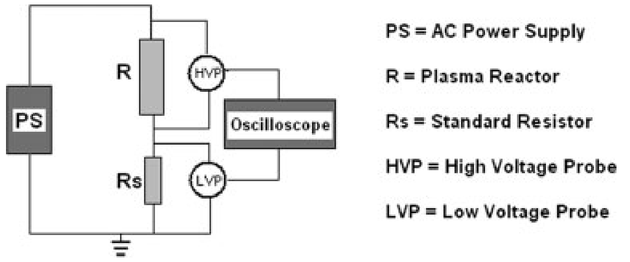

Figure 2. Circuit setup used for DBD plasma reactor control and measurement.

In-site H_2O_2 synthesis and propene epoxidation

The feed gas (105 ml/min) of the DBD reactor consisted of H_2 and O_2. The content of O_2 was controlled at 4.8 vol.%, which was chosen to be outside the flammable and explosive range. The residence time of the feed gas in the discharge zone was 18 s. The DBD reactor worked at ambient conditions (0.1 MPa, 15–25 °C). First, H_2 and O_2 were fed to the DBD reactor, then the synthesis of H_2O_2 was started by applying an alternating current high-voltage to the DBD reactor. The products of the DBD reactor, H_2O_2 and H_2O, were absorbed by methanol (30 ml) in a collector connected to the exit of the DBD reactor, and then the H_2O_2-methanol solution in the collector was fed to the epoxidation reactor for PO synthesis. To obtain a stable H_2O_2-methanol solution, fresh methanol was fed into the collector to maintain the volume of solution at 30 ml. The flow rate of methanol pumped into the collector was 1.2 ml/h more than that of the H_2O_2-methanol solution pumped out of the collector. The flow rate difference was designed to compensate the amount of methanol being carried off by the effluent gas (H_2 and O_2). When

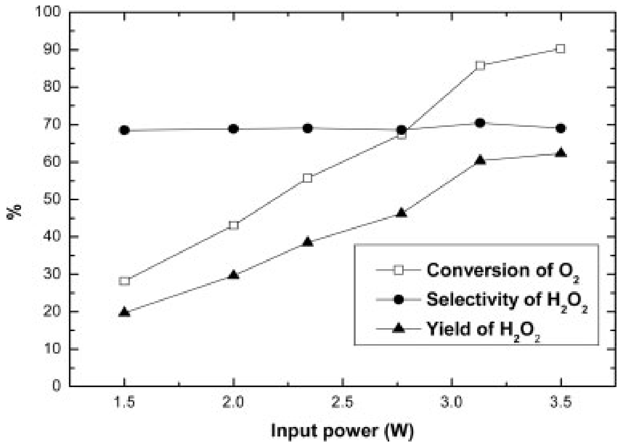

Figure 3. Performance of the DBD reactor in the direct synthesis of H_2O_2 from H_2/O_2 mixture (0.1 MPa, room-temperature, flow rate of feed gas 105 ml/min, O_2 content of feed gas 4.8 vol.%).

the input power of the DBD reactor was fixed, the concentration of H_2O_2 in the collector would reach an equilibrium value after a period of discharge and operation. Altering the flow rates of compensating methanol and output H_2O_2-methanol solution would influence the ultimately equilibrium concentration of H_2O_2 in the collector.

The fixed-bed reactor for the epoxidation of propene was loaded with 3 g egg shell-like catalyst ,which was prepared by the method reported in literature.[18] The core of the catalyst was an inert silica-alumina ball, the shell of the catalyst was a 0.3–0.4 mm TS-1 lamina. The average content of TS-1 in the egg shell-like catalyst was about 30%. Before use, the catalyst was activated in a muffle in air at 550 °C for 1 h. After the load of the catalyst, the fixed-bed reactor was preheated to desired temperature by water-jacket. When H_2O_2-methanol solution and propene were fed into the TS-1 bed at 3 MPa, the epoxidation of propene took place via a liquid-solid phase reaction mode.

Product analysis

The effluent gas from the DBD reactor was analyzed by an online gas chromatography equipped with a TCD detector and a molecular sieve column (2.0 m × 2 mm) containing the stationary phase GDX502. Liquid samples from the fixed-bed reactor were analyzed by another gas chromatography equipped with a FID detector and a capillary column (40.0 m × 0.25 mm) containing poly(ethylene glycol) 20 M as the stationary phase. The concentration of H_2O_2 was determined by iodiometric titration. In the synthesis process of hydrogen peroxide, H_2O_2-yield of the DBD reactor was calculated based on oxygen.

H_2O_2 conversion, PO selectivity and PO yield were used to assess the performance of the epoxidation of propene. PO yield was based on H_2O_2 and took the utilization rate of H_2O_2 into account. PO selectivity was based on all organic products (molar amount of produced PO to molar amount of all organic products).

Results and Discussion

In-site preparation of H_2O_2-methanol solution by plasma method

First of all, the performance of the DBD reactor for the direct synthesis of H_2O_2 via the nonequilibrium plasma reactions of H_2/O_2 was investigated. Figure 3 indicates that the conversion of O_2 increased monotonously with input power, the selectivity to H_2O_2 kept constant around 69%, consequently, the yield of H_2O_2 increased with the conversion of O_2. When the input power was fixed at 3.5 W, the conversion of O_2, and the yield of H_2O_2 reached 90% and 62%, respectively. Figure 4 indicates that when the input power was fixed at 3.5 W, the concentration of H_2O_2 in the collector increased linearly with the discharge time. About 2.5 h after the start of the discharge, the concentration of H_2O_2 in the collector reached 0.70 mol/L (2.98 wt.%). Then fresh methanol was continuously fed into the collector at a flow rate of 13.2 ml/h, at the same time the H_2O_2-methanol solution (0.70 mol/L H_2O_2) was taken out of the collector at a flow rate of 12 ml/h, so the concentration of H_2O_2 in the collector was able to keep stable at 0.70 mol/L. Thereafter, an H_2O_2-methanol solution containing 0.70 mol/L H_2O_2 would be supplied continuously for the epoxidation reactor at the flow rate of 12 ml/h.

By employing this plasma method on the DBD reactor, it is easy to directly produce H_2O_2-methanol solution with higher H_2O_2 concentration from the mixture of H_2 and O_2. Table 1 indicates that, when the predischarge time of the DBD reactor increased to 5 h, 7.5 h and 10 h, the concentration of H_2O_2 in the output H_2O_2-methanol solution increased to 5.46 wt.% (1.29 mol/L), 7.89 wt.% (1.88 mol/L) and 10.14 wt.% (2.44 mol/L), respectively. As the H_2O_2 concentration of the output H_2O_2-methanol solution increased, the flow rate of the H_2O_2-methanol solution decreased because the productivity of H_2O_2 of the DBD reactor under given conditions kept constant during a continuous discharge. That is, to obtain concentrated H_2O_2-methanol solution with plasma method, we only need to allow the DBD reactor a

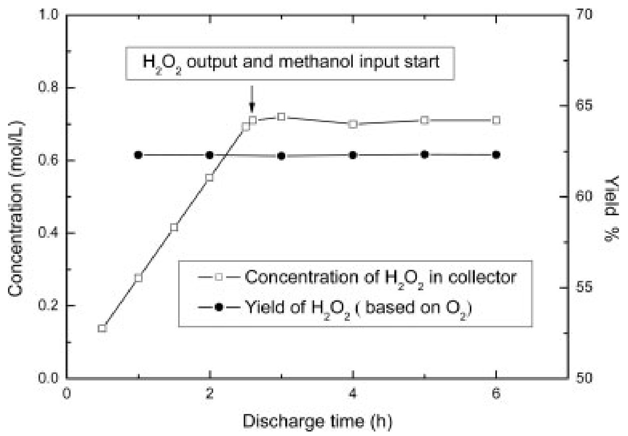

Figure 4. In-site preparation of the H_2O_2-methanol solution during the continuous discharge of the DBD reactor (input power 3.5 W, 0.1 MPa, room-temperature, flow rate of feed gas 105 ml/min, O_2 content of feed gas 4.8 vol.%).

Table 1. Direct Generation of High Concentration H_2O_2 Solution from H_2 and O_2 via Nonequilibrium Plasma Reactions

	DBD reactor performance		H_2O_2-methanol solution continuously output after predischarge		
Predischarge time, h	X_{O_2}, %	$S_{H_2O_2}$, %	$C_{H_2O_2}$, wt.%	Composition, wt. H_2O_2:H_2O:MeOH	output rate, ml/h
2.5	90	69	2.86	0.71:0.34:23.74	12.4
5.0	90	69	5.46	1.41:0.67:23.74	6.4
7.5	90	69	7.89	2.12:1.01:23.74	4.4
10.0	90	69	10.14	2.83:1.35:23.74	3.4

Nonequilibrium plasma reaction conditions: DBD reactor input power 3.5 W, AC power supply frequency 14 kHz, flow rate of feed gas 105 ml/min, O_2 content of feed gas 4.8 vol.%, room-temperature, 0.1 MPa.

longer predischarge time and transfer the H_2O_2-methanol solution at lower flow rate. Unlike in the direct synthesis of H_2O_2 catalyzed by supported noble metal catalysts (Pd, Au, etc.),[19–25] where the catalysts and the H_2/O_2 mixture (O_2 in excess) are dispersed into acidified solvents (ca. water, methanol), and the direct synthesis of H_2O_2 is conducted in liquid-phase, the production of concentrated H_2O_2 solution is handicapped by the decomposition of H_2O_2 by the same supported noble metal catalysts even if conditions of high-pressure (ca. 3.7 MPa) and low-temperature (ca. 2 °C) are employed, and/or decomposition inhibitors like sodium bromide (also a contamination to the H_2O_2 solution) are added. In the direct synthesis of H_2O_2 by the plasma method, where H_2O_2 and H_2O were produced in gas-phase in the discharge zone of the DBD reactor under atmospheric pressure and room-temperature (without using any solvent and catalyst) via the free-radical reactions of nonequilibrium plasma of H_2 and O_2, as soon as the H_2O_2 was formed it was taken away from the discharge zone by unreacted H_2 and O_2 gases (residence time $\tau = 18$ s), and collected in a separated collector. Thus, the decomposition of H_2O_2 by the impacts of energetic electrons was effectively reduced, and the selectivity and yield of H_2O_2 were not affected by the collection of concentrated H_2O_2 solution.

The safety of the plasma method was guaranteed by the composition of the H_2/O_2 mixture. According to literature, the explosion and ignition limit of H_2/O_2 mixture is inbetween 6–96 mol.% O_2, and it changes under some conditions.[25] For example, the increase of the reaction pressure will widen the explosive limit of H_2/O_2 mixture. In this study, the DBD reactor was operated under atmospheric pressure and a H_2/O_2 mixture of 4.8 mol.% O_2 was used as the feed of the DBD reactor. This H_2/O_2 mixture was proved to be safe. Fortunately, high H_2O_2 selectivity (69% based on oxygen atom) could be obtained with such a nonexplosive, low oxygen H_2/O_2 mixture. Our experiments also indicated that, unless O_2 in the feed of the DBD reactor was completely consumed under high-input power, the selectivity of H_2O_2 would not be decreased by the content of O_2 in H_2/O_2 feed. In fact, the selectivity of H_2O_2 of the plasma method was mainly influenced by the structure of the discharge reactor.[16,26] Generally speaking, the merits of safety, simplicity and high-selectivity of the plasma method in directly generating concentrated H_2O_2 solution from H_2 and O_2, make it an attractive candidate for the in-site supply of H_2O_2. Currently, the energy efficiency of H_2O_2 generated by the plasma method is about 80.8 g/kWh, it should be advanced as high as possible from the view of practice.

Epoxidation of propene over TS-1 catalyst with in-site H_2O_2

In order to select suitable reaction conditions, the influences of the reaction temperature, the concentration of H_2O_2-methanol solution (C_{H2O2}), the molar ratio of propene/H_2O_2 ($C_3^=/H_2O_2$), and the total feed velocity ($WHSV_{Total}$, the total feed included H_2O_2-methanol solution and propene) on the epoxidation of propene were investigated. As shown in Table 2, under the conditions of $C_{H2O2} = 0.70$ mol/L, H_2O_2/methanol $= 0.03$ (mol ratio), $C_3^=/H_2O_2 = 4.2$, $WHSV_{Total} = 3.7\ h^{-1}$, and the reaction pressure = 3.0 MPa, when the liquid-phase epoxidation of propene with in-site H_2O_2-methanol solution prepared by DBD reactor was carried out at 40 °C, the conversion of H_2O_2 (X_{H2O2}), the selectivity of PO (S_{PO}) and the yield of PO based on H_2O_2 (Y_{PO}) were about 80%, 93% and 50%, respectively. The identified byproducts, mainly propene glycol and mono-methyl ether of propene glycol, were resulted from the secondary reactions of pro-

Table 2. Influence of Reaction Conditions on Epoxidation Reaction

	Epoxidation conditions				Epoxidation performance		
Run	t, °C	$C_{H_2O_2}$, mol/L	$C_3^=/H_2O_2$, mol	$WHSV_{Total}$, h^{-1}	$X_{H_2O_2}$, %	S_{PO}, %	Y_{PO}, %
1	40	0.70	4.2	3.7	80.3	93.2	50.4
2	45	0.70	4.2	3.7	82.4	92.5	62.8
3	50	0.70	4.2	3.7	93.0	94.2	67.8
4	55	0.70	4.2	3.7	95.9	88.1	60.8
5	50	0.96	4.2	2.8	92.7	95.8	60.6
6	50	0.56	4.2	4.4	88.6	95.1	72.8
7	50	0.70	4.9	3.8	94.3	92.1	71.9

Nonequilibrium plasma reaction conditions: DBD reactor input power 3.5 W, AC power supply frequency 14 kHz, flow rate of feed gas 105 ml/min, O_2 content of feed gas 4.8 vol.%, room-temperature, 0.1 MPa.
Epoxidation reaction conditions: catalyst 3 g, 3 MPa.

Table 3. Operation Stability of the Novel Integrated PO-Synthesis Process

	DBD reactor		Epoxidation reactor		Epoxidation results		
TOS/h	H_2O_2 solution output, ml/h	$C_{H_2O_2}$ mol/L	$C_3^=/H_2O_2$ mol ratio	$WHSV_{Total}$ h^{-1}	$X_{H_2O_2}$ %	S_{PO} %	Y_{PO} %
3	12	0.70	4.2	3.7	93.0	94.2	67.8
6	12	0.70	4.2	3.7	92.5	94.2	67.0
9	12	0.70	4.2	3.7	93.7	94.6	66.2
12	12	0.70	4.2	3.7	92.3	94.8	67.9
15	12	0.70	4.2	3.7	92.2	93.9	68.7
18	12	0.70	4.2	3.7	92.5	94.6	67.7

DBD reactor: room-temperature, 0.1 MPa, input power 3.5 W, AC power supply frequency 14 kHz, flow rate of feed gas 105 ml/min, O_2 content of feed gas 4.8 vol.%.
Epoxidation reactor: catalyst 3 g, temperature 50 °C, pressure 3 MPa.

pene oxide. When the temperature increased, the conversion of H_2O_2 increased steadily and approached 96% at 55 °C. The selectivity of PO, however, maintained around 93–94% within 50 °C and remarkably decreased to 88% at 55 °C. As a result the yield of PO based on H_2O_2 increased to about 68% at 50 °C, but declined to about 61 % at 55 °C. It was found that the increases of byproducts via epoxide ring opening reactions were the main causes of the PO selectivity decrease. It seemed that 50°C was a suitable temperature for the epoxidation of propene here. Under the conditions of 50 °C and $C_3^=/H_2O_2$ molar ratio = 4.2, the increase of the H_2O_2-methanol solution concentration from 0.70 mol/L to 0.96 mol/L (H_2O_2/methanol = 0.04) was accompanied by the decrease of the total feed velocity ($WHSV_{Total}$) from 3.7 h^{-1} to 2.8 h^{-1} (less methanol). Such changes had little influence on the conversion of H_2O_2 and the selectivity of PO, but the yield of PO declined from about 68% to about 61%. This meant that the epoxidation of propene with H_2O_2-methanol solution of too high H_2O_2 concentration mainly favored the decomposition of H_2O_2. On the other hand, the decrease of the H_2O_2-methanol solution concentration from 0.70 mol/L to 0.56 mol/L (H_2O_2/methanol = 0.023) was accompanied by the increase of the total feed velocity from 3.7 h^{-1} to 4.4 h^{-1}. Such changes also had little influence on the selectivity of PO, but the conversion of H_2O_2 declined significantly while the yield of PO notably increased. This might be attributed to the restraining effect of the diluted H_2O_2-methanol solution on the decomposition of H_2O_2. In this study, we chose C_{H2O2} = 0.7 mol/L as the proper concentration of H_2O_2-methanol solution. It might be seen that, under the conditions of C_{H2O2} = 0.70 mol/L, H_2O_2/methanol = 0.03, $C_3^=/H_2O_2$ = 4.2, $WHSV_{Total}$ = 3.7 h^{-1}, reaction temperature = 50 °C, and reaction pressure = 3.0 MPa, our integrated PO-synthesis process, based on the in-site DBD plasma H_2O_2 worked with very high H_2O_2 conversion (ca. 93%), and PO selectivity (ca. 94%). The relatively low PO yield (ca. 68%), based H_2O_2 was mainly resulted from the decomposition of H_2O_2, which was obviously related to the TS-1 catalyst, and the epoxidation reactor used. In addition, the increase of the molar ratio of $C_3^=/H_2O_2$ seemed to be a helpful means for improving the yield of PO.

The possibility of the novel PO-synthesis process for long time-on-stream operation was investigated over an 18-h course. As shown in Table 3, when the DBD reactor for the direct synthesis of H_2O_2 operated under the conditions of room-temperature, 0.1 MPa, input power = 3.5 W, AC power supply frequency = 14 kHz, flow rate of the H_2/O_2 mixture = 105 ml/min, O_2 content of the H_2/O_2 mixture = 4.8 vol.%, it could steadily supply a H_2O_2-methanol solution of 0.70 mol/L H_2O_2 at a flow rate of 12 ml/h (fresh methanol compensation rate for the collector 13.2 ml/h) for the epoxidation of propene. Thus, when the feed of propene was controlled at $C_3^=/H_2O_2$ = 4.2, the epoxidation reactor (reaction temperature 50 °C, reaction pressure of 3.0 MPa) could then work at $WHSV_{Total}$ = 3.7 h^{-1}, and H_2O_2/methanol = 0.03. Within the time course investigated, both reactors operated smoothly, the results of the propene epoxidation kept at 92–93% H_2O_2 conversion, 94–95 % PO selectivity and 66–69% PO yield. These results show that the in-site supply of H_2O_2 for the TS-1 catalyzed epoxidation of propene via the direct reactions of H_2/O_2 nonequilibrium plasma in a DBD reactor is technically viable.

Conclusions

This study shows that, the direct synthesis of H_2O_2 by transforming a H_2/O_2 mixture into nonequilibrium plasma on dielectric barrier discharge (DBD) reactor is a very promising in-site H_2O_2 strategy for the epoxidation of propene. It is characterized by the gas-phase synthesis of H_2O_2. Mass-transfer limitation associated with supported palladium catalysts is completely avoided. So that H_2O_2 can be generated at high-selectivity and high-rate under atmospheric pressure and room-temperature, pure and concentrated H_2O_2 solution can be easily obtained without using any purification/concentration operations. The employment of methanol as H_2O_2 absorbent (methanol does not enter the DBD plasma reactor) facilitates the integration of the DBD reactor (for H_2O_2 synthesis) with titanium silicalite (TS-1) fixed-bed reactor (for propene oxide synthesis), because methanol is also the best solvent for propene epoxidation. Practically, methanol is very easy to be recycled from the downstream separation units to the up-stream reaction units. The simplicity of the integrated process makes it easy to be operated and scaled-up. This in-site H_2O_2 strategy might also be applicable for other selective oxidation reactions. Our future work will be focused on the improvement of the H_2O_2 synthesis efficiency, especially the energy efficiency.

Acknowledgments

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