Development of New Propylene Oxide Process

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There has always been a strong demand for the development of a new PO-only process. Conventional processes –the chlorohydrin PO-only process and the organic hydroperoxide process, which generates a huge amount of co-products– have given PO producers headaches due to the generation of waste that is not environmentally friendly and the dependence of product price on the fluctuating market for co-products.

With the development of a high performance titanium epoxidation catalyst by our researchers, we have succeeded in establishing a novel PO-only manufacturing process where cumene acts as the oxygen carrier.

The new PO Cumene process is considered a "green process" since it gives higher yields than conventional processes while only producing small amounts of by-products.

Introduction

Propylene oxide (PO) is a major industrial product with production of more than 6 million tons per year worldwide. Approximately 70% of it is used as polypropylene glycol in the raw materials for urethane, and the remainder is used as propylene glycol in the raw materials for unsaturated polyesters, food product additives and cosmetics (**Fig. 1**). The demand for urethane is growing remarkably, particularly in Asia, a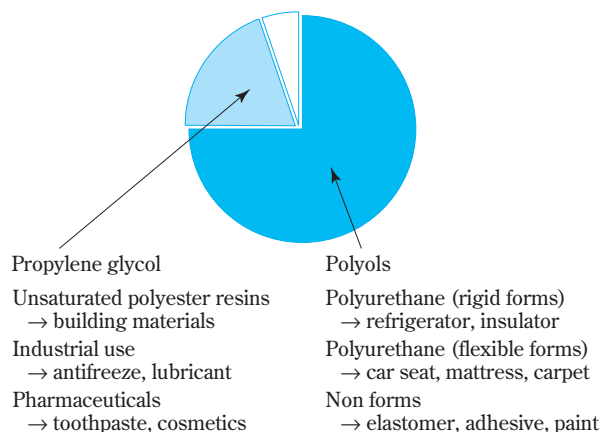nd one PO producer after another is announcing business plans for new plants (**Fig. 2**). Production by the principle producers of PO worldwide is shown in **Fig. 3**, and **Fig. 4** shows the proportions of production by production method.

PO production methods that have been industrialized up to this point can be roughly divided into two methodologies. The first is PO-only production methods using chlorine, and the other is co-production methods that produce co-products such as styrene monomers along with the PO. All of the industrial processes that have been implemented up to now carry
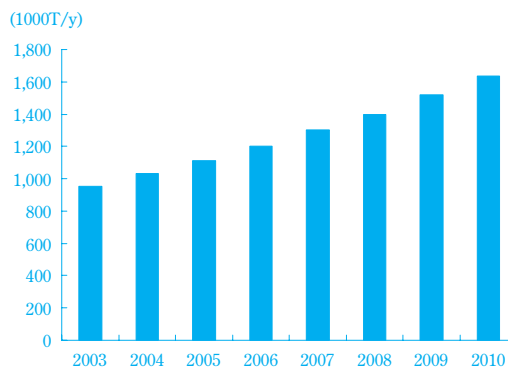

Propylene glycol
Unsaturated polyester resins
   → building materials
Industrial use
   → antifreeze, lubricant
Pharmaceuticals
   → toothpaste, cosmetics

Polyols
Polyurethane (rigid forms)
   → refrigerator, insulator
Polyurethane (flexible forms)
   → car seat, mattress, carpet
Non forms
   → elastomer, adhesive, paint

Fig. 1　Uses for Propylene oxide (PO)

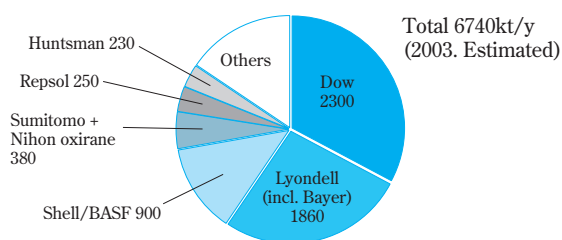**Fig. 2**　Asian PO demand forecasting (excluding Japan)

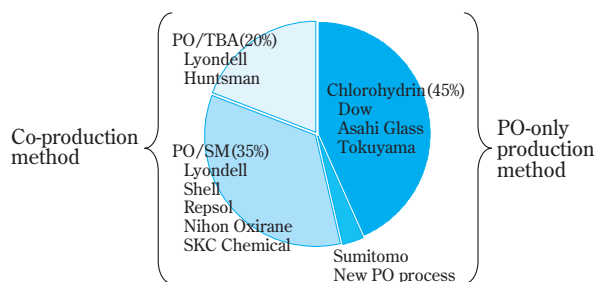**Fig. 3** Global PO supplier and capacity (1000t/y)

Fig. 4 PO production technologies

with them the problem of byproducts and the problem of controlling market conditions and the like for the co-products, and the PO producers in various countries have been focusing the attention on developing a new PO-only method.

Sumitomo Chemical has also been eagerly researching new PO-only production methods. Taking the opportunity of our successfully developing a new epoxidation catalyst in 1998, we were successful in establishing the technology for a new PO production process, and starting in 2003, we began using the new PO-only production method at 150,000 tons per year at our Chiba Plant. After this, we implemented a plant enhancement to 200,000 tons per year in the fall of 2005 based on the healthy demand in Asia, and operations are continuing to go well. Furthermore, we plan to start operating a second plant (200,000 tons of PO per year) in 2008 according to the Rabigh plan for Saudi Arabia.

Along with reviewing the current industrial processes, this paper introduces the features of the PO-only process developed by Sumitomo Chemical.
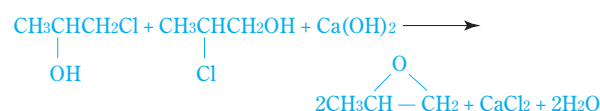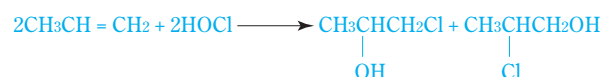
Existing PO Production Processes

The propylene oxide (PO) production processes that have been industrialized so far can be roughly divided into the chlorine method, which is a PO-only method, and the organic peroxide method, which is a co-pro-

duction method. Each of these production methods will be introduced in the following.[1, 2]

1. Chlorine Method

The chlorine method (also known as the chlorohydrin method) is technology that was originally used for the production of ethylene oxide, but in the 1960s, with the conversion of production methods to direct oxidation methods for ethylene oxide, it became the method used for producing PO using the idle plants. The largest producer using this method is the Dow Chemical Company, and there are two Japanese producers, Asahi Glass Co. Ltd. and Tokuyama Corp. Up to now, this was the only industrial PO-only production method.

$$2CH_3CH = CH_2 + 2HOCl \longrightarrow \underset{\underset{OH}{|}}{CH_3CHCH_2Cl} + \underset{\underset{Cl}{|}}{CH_3CHCH_2OH}$$

$$\underset{\underset{OH}{|}}{CH_3CHCH_2Cl} + \underset{\underset{Cl}{|}}{CH_3CHCH_2OH} + Ca(OH)_2 \longrightarrow$$
$$2CH_3CH \underset{\underset{O}{\diagdown\diagup}}{—} CH_2 + CaCl_2 + 2H_2O$$

Propylene and chlorine are reacted to produce a mixture of α- and β-chlorohydrin (9:1), and next, PO is synthesized by reaction with an alkali (calcium hydroxide, for example). The only product is PO, and as a byproduct, an alkali salt is produced in the same molar quantity as the PO. This production method is a moderate temperature reaction in an aqueous solution, but for each ton of PO, a large amount of secondary raw materials, 1.4 tons of chlorine and one ton of calcium hydroxide, are necessary, and approximately 2.0 tons of calcium chloride is produced as a byproduct. In addition, a large excess of water is present in this reaction, and a chlorohydrin concentration of 3–6% is maintained, so the formation of chlorine adducts must be controlled. Therefore, a large volume of waste water containing the alkali salt is produced (a volume several tens of times that of the PO), and the process is one with an extremely large waste water burden.

2. Organic Peroxide Method

The organic peroxide method (also known as the hydroperoxide method) was first developed by Halcon Corp. and Atlantic Richfield Oil Corp. (later ARCO) in the 1970s. In this method there is a method using ethylbenzene and a method using isobutane, and in each of them PO is synthesized by indirect epoxidation of

propylene using ethylbenzene hydroperoxide or tert-butyl hydroperoxide as the organic peroxide. A styrene monomer (SM) or tert-butanol (TBA) is produced as the co-product. Typical producers using PO/SM co-production are Lyondell Chemical Company and Shell Chemicals Ltd., and in Japan, there is only Nihon Oxirane Co., Ltd. The PO/TBA producers are Lyondell and Huntsman International LLC. In a reflection of the trends in demand for the two sets of co-products in recent years, new PO plants have exclusively employed the PO/SM co-production method. We will describe the PO/SM co-production process in the following.
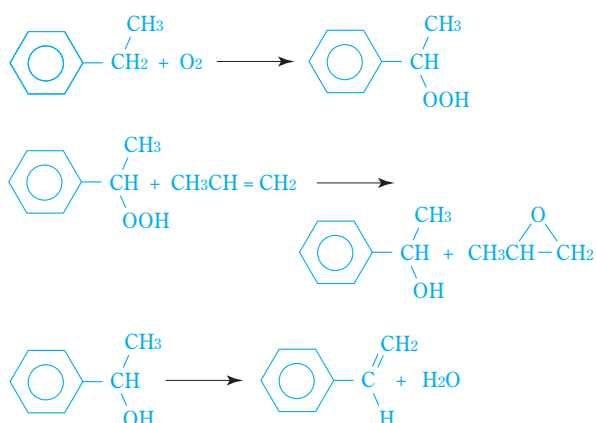
First of all, ethylbenzene hydroperoxide is produced by air oxidation of ethylbenzene. Next, the ethylbenzene hydroperoxide and propylene are reacted in the presence of an epoxidation catalyst, and α-methylbenzyl alcohol and PO are produced. The α-methylbenzyl alcohol that is produced undergoes a dehydration reaction in the presence of an acid catalyst to form SM. Mo based homogeneous catalysts[3] and Ti supported silica based heterogeneous catalysts[4, 5] are used for the epoxidation catalyst. With the isobutane method, there is co-production of TBA. If TBA is dehydrated, it forms isobutylene, and if it is further reacted with methanol, methyl tertiary-butyl ether (MTBE), which is useful as a gasoline additive, can be synthesized.

These organic peroxide methods use the oxidative power of hydroperoxides skillfully and have the superior characteristic of not requiring the secondary raw materials such as chlorine. However, with the ethylbenzene method, approximately 2.5 tons of styrene is co-produced for every ton of PO, and with the isobutane method, 2.1 tons of isobutylene is co-produced for each ton of PO. Since these co-products are severely affected by market conditions, it is difficult to say that these are always the optimal methods for producing PO.

Sumitomo Chemical's New PO-only Process

Using cumene, Sumitomo Chemical has established a cumene PO-only process as a new PO production process. We developed a high performance Ti based epoxidation catalyst in 1998, and taking this as an opportunity, we started working on developing a new PO-only process using cumene. Starting with the laboratory investigations in 1999, it was possible to carry out development and establish the business in a short time by maximizing the use of concurrent engineering, with bench tests in 2000, pilot testing in 2001, completion of a plant in 2002 and plant startup in 2003.

This production method is fundamentally similar to the organic peroxide methods, but the major feature is using a high performance epoxidation catalyst that uses cumene as the reaction medium, so we can call it the cumene PO-only process. This production method is made up of the following processes.

(1) Oxidation process where cumene is oxidized in air to obtain cumene hydroperoxide (CMHP).
(2) Epoxidation process where α,α-dimethyl benzyl alcohol (CMA) is obtained from CMHP and propylene in the presence of an epoxidation catalyst.
(3) Hydrogenation process where CMA is hydrogenated and cumene is obtained in the presence of a hydrogenation catalyst and hydrogen.
(4) Cumene purification process where the cumene obtained is purified and recycled to the oxidation process.
(5) PO purification process where PO is purified.

Three reaction processes are included, the (1) oxidation process, (2) epoxidation process and (3) hydrogenation process. In the following, we will give an overview of each of the reaction processes.

1. Oxidation Process

This is a process where cumene is oxidized by oxygen and cumene hydroperoxide (CMHP) is obtained.
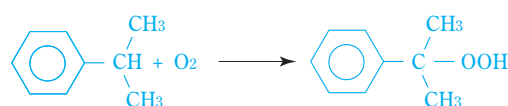
The oxidation reaction is an auto-oxidation reaction that occurs without a catalyst, and the technology is basically the same as phenol synthesis by the cumene method. Sumitomo Chemical has built up its own emulsion oxidation technology in the production of

cresol (cymene oxidation) and resorcin (meta dicumene oxidation), and we have made maximum use of this knowledge. According to references, the cumene oxidation rate is known to be approximately seven times faster than the ethylbenzene oxidation rate.[6] In addition, since cumene hydroperoxide is basically a stable peroxide, the hydroperoxide yield is higher than that for ethylbenzene oxidation and isobutane oxidation. However, it was also possible to establish both a high reaction rate and a high hydroperoxide yield through precise control of sodium carbonate and other alkaline water quantities. In addition, it is well known that a small amount of a phenol typically works to inhibit the oxidation reaction in auto-oxidation, and in the cumene oxidation reaction it is also important to have a grasp on the effects of impurities. We examined the various types of impurities in detail in laboratory experiments. Based on these results, the recycled cumene was supplied to the oxidation process after undergoing a prescribed purification to eliminate phenols and the like. As was mentioned previously, the cumene oxidation is a comparatively rapid reaction, and the prescribed CMHP cumene solution is obtained, so there is not need for a high level hydroperoxide concentration operation like that carried out in phenol production.

2. Epoxidation Process

This is a process where CMHP and propylene are reacted and α,α-dimethyl benzyl alcohol (CMA) is obtained.
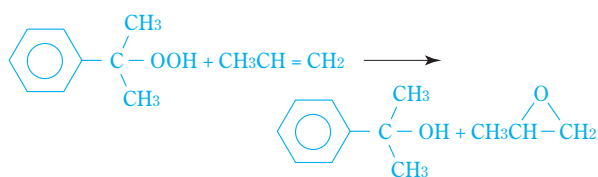

It is a fixed bed process that uses a Ti-silicon oxide catalyst developed by Sumitomo Chemical. An excess of propylene is used to increase the reaction rate, and the unreacted propylene is recovered after this processed and recycled. It is possible to carry out the reaction at a comparatively mild temperature because of the use of the highly active Ti epoxidation catalyst and the good stability of the cumene hydroperoxide, and we have achieved extremely high reaction rates. We will discuss the development of the catalyst later. Optimal reaction vessel design and operating condi-

tions are used in this process, based on the clarification of the reaction kinetics for the epoxidation reaction and the other various secondary reactions that was done in laboratory experiments. This epoxidation reaction is an exothermic reaction, and the temperature rises from the reactor inlet to the outlet. An excess temperature rise problematically increases the side reactions of CMHP thermal decomposition and consecutive reactions of PO, so there is a division into multiple catalyst layers, and the reaction temperature is adjusted by having heat exchangers between the various catalyst layers. After the propylene has been recovered from the epoxidation reaction solution, distillation is used to separate it into a crude PO (light stream) and a CMA/cumene solution (heavy stream).

3. Hydrogenation Process

This is a process where cumene is reproduced from α,α-dimethyl benzyl alcohol (CMA) and hydrogen.
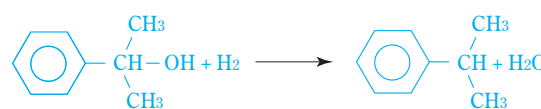
Since CMA is a type of benzyl alcohol and has high reactivity, the hydrogenation reaction progresses easily with various metal catalysts. In addition, since CMA is a bulky compound with another methyl group attached in an α position to the α-methyl benzyl alcohol discussed earlier, it has the characteristic of side reactions such as dimerization under high temperature conditions not occurring easily. Therefore, the conversion to cumene can be done in an almost completely quantitative manner with this process. The reaction is a normal fixed bed process where the bed is packed with a hydrogenation catalyst, and it is carried out by supplying the CMA/cumene solution and hydrogen. This reaction is also an exothermic reaction, and the heat energy from the reaction can be recovered and used. The operating conditions are optimized considering the reaction yield aspect and the thermal energy efficiency. In this process, CMA is converted to cumene, and next, it is recovered after passing through some separation and purification processes including oil and water separation.

As described above, the salient characteristic of this process is the large cycle with cumene as the oxygen carrier, and using the highly active epoxidation catalyst and the good stability of cumene and its derivatives

(including cumene hydroperoxide and α,α-dimethyl benzyl alcohol), we have taken into consideration holding the cumene loss to a minimum overall. The reason that the cumene cycle was established in an economical manner producing PO, was truly this minimizing of the cumene loss. Furthermore, we created a design that effectively used the reaction heat in the oxidation, epoxidation and hydrogenation processes, and minimized the energy in separation and purification. In total, it is a process with very little energy consumption. **Table 1** compares Sumitomo Chemical's cumene method and existing PO processes. Compared with existing methods, Sumitomo Chemical's cumene method has a high propylene yield and can be called an environmentally friendly green process with almost no byproducts.

| **Table 1** | Comparison of commercial PO production processes |

Process	1st generation (1910~) Chlorohydrin method	2nd generation (1960~) PO/SM Co-production	3rd generation (2003~) Sumitomo PO only production
Oxidate source	Chlorine	Ethylbenzene	Cumene
Byproduct & its production (t/t-PO)	CaCl₂ 2.0	Stylene 2.5	– ~ 0
Propylene selectivity	Low	Low	High

Development of Epoxidation Catalyst

The most important thing in the construction of this process was the development of the epoxidation catalyst. The concept for this PO-only method where cumene is cycled as in this process was recognized back in the 1960s,[7] but one can assume that one of the reasons it was not achieved until now was there being no high performance epoxidation catalyst that could be used economically. In other words, since the cumene loss is large in epoxidation processes with conventional homogeneous Mo catalysts and the like, the processes could not be set up economically.

In epoxidation reactions for olefins using peroxides, the various conventional metals (Mo, V, W, Cr, Ti, Mn, Ru and the like) are active, and among these, titanium based catalysts in combination with silica are known to exhibit a high level of epoxidation activity. In terms of the Ti silica catalysts that we have investigated up to this point, there are Ti silicate zeolite catalysts, titania

silica oxide catalysts, Ti supported silica catalysts and the like. In particular, it is known that the Ti silicate catalysts have remarkably high epoxidation activity because they have a high dispersion of highly active tetrahedral titanium in a highly hydrophobic crystalline silica matrix.[8]–[12] However, the activity of these conventional Ti silica catalysts varies greatly according to peroxides, olefins or solvent systems used, and in particular, there were none that exhibited a high level of activity for epoxidation of large molecules like CMHP.

The epoxidation catalyst developed by Sumitomo Chemical is a silicon oxide catalyst that contains Ti (called Sumitomo Ti catalyst in the following) and has a mesoporous structure. It was designed to exhibit a high level of activity for large molecules like CMHP. This mesoporous catalyst, which is prepared using a sol-gel process, was the first of its kind in the world to be used industrially. The three elements shown in **Fig. 5** are important as the main points for increasing the performance can be thought of as follows. (1) The tetrahedral titanium, which is highly active in epoxidation reactions, is in the silica matrix in a highly dispersed state. (2) The meso–macro pores are precisely controlled so large molecules like CMHP can be sufficiently diffused, and (3) propylene affinity is increased by giving sufficient hydrophobic properties. In particular, as a result of many keen examinations of how to create as many mesoporous pores, which are effective for the reaction, as possible, we were able to achieve a high activation of 30 times the initial one by precisely controlling the sol-gel preparation process and boldly changing the ideas for the after processing that followed. In addition, we added our own special ingenuity in the molding processes and were able to produce a solid catalyst with high strength that can stand up to practical use. By the way, the Ti silicate catalyst (TS-1) known to be highly active in the hydrogen peroxide method for PO synthesis that will be described later only has micropores of 5–6Å, and the reaction activity for large molecules like CMHP was extremely low (**Fig. 6**). The Sumitomo Ti catalyst has developed mesopores on a nanometer scale, and therefore, its major characteristic is the fact that the surface area that can be used effectively for the CMHP epoxidation reaction is remarkably large (**Fig. 7**). **Fig. 8** shows the an XAFS analysis of the Sumitomo Ti catalyst, and one can see that tetrahedral titanium, which has a high epoxidation activity, is present, and octahedral titani-

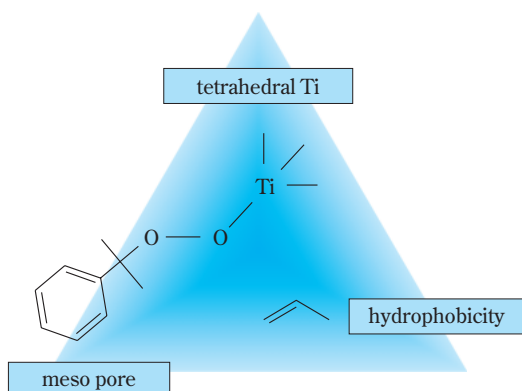um, which is inactive in epoxidation, is hardly present at all.

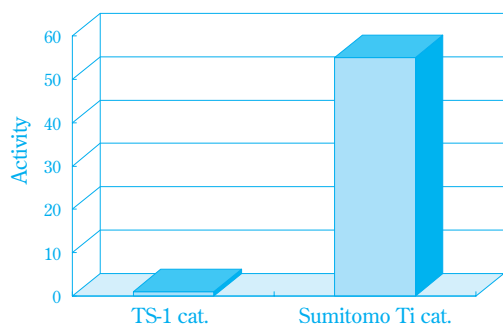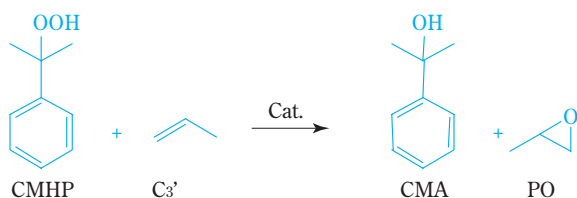**Fig. 5** Important factors for effective Ti epoxidation catalyst

Fig. 6 Comparison of C3'/CMHP epoxidation activity between TS-1 catalyst and Sumitomo Ti catalyst
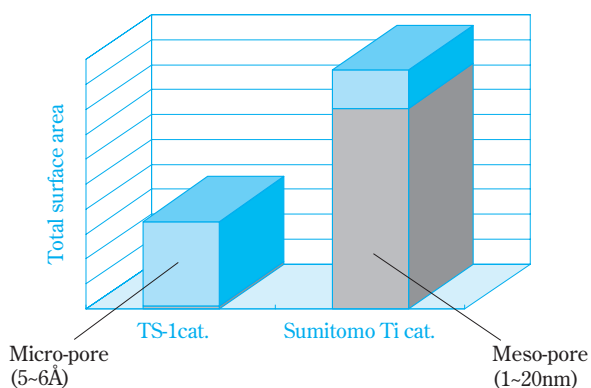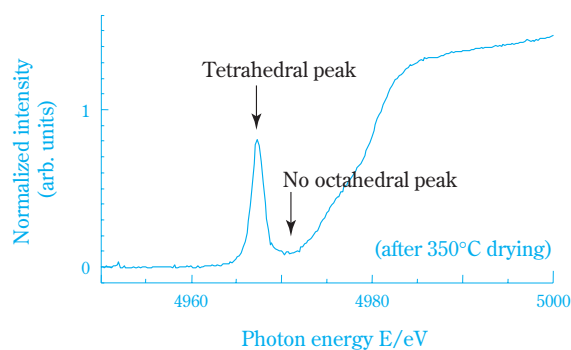

Fig. 7 Comparison of micro/meso pore structure between TS-1 catalyst and Sumitomo Ti catalyst

Ti coordination state : Tetrahedral → active site
Octahedral → inactive site

Fig. 8 XAFS spectroscopy of Sumitomo Ti catalyst

Comparison with Other PO-only Methods

Besides Sumitomo Chemical, various producers are actively developing new PO-only processes. A list of the processes being developed is given in **Table 2**. There are many processes such as a hydrogen peroxide method, an in-situ hydrogen peroxide method carried out while hydrogen peroxide is being synthesized in a liquid phase from hydrogen and oxygen, and a direct oxidation method where there is a reaction with propylene, hydrogen and oxygen or propylene and oxygen in the gas phase.[13)-16)] The direct oxidation method has problems with a low conversion and a short catalyst life, and the in-situ hydrogen peroxide method has problems with low productivity. Of these, the PO production method that uses hydrogen peroxide is seen as being the closest to industrialization.

Table 2 Newly developing PO production processes

Process & typical example	company
Hydrogen peroxide (by Anthraquinone) route $C_3' + H_2O_2 \rightarrow PO + H_2O$ TS-1 cat., MeOH solv.	Dow(Enichem)/ BASF/Solvay/ Degussa/Uhde
In-situ hydrogen peroxide route $C_3' + H_2 + O_2 \rightarrow PO + H_2O$ Pd/TS-1 cat., MeOH solv.	Lyondell, BASF
Vapor phase direct oxidation route $C_3' + H_2 + O_2 \rightarrow PO + H_2O$ $C_3' + \frac{1}{2} O_2 \rightarrow PO$ Au/TS-1, Ag/CaCO$_3$ etc.	Dow, BASF, Bayer, Lyondell, NipponShokubai

Fig. 9 compares the production processes for the Sumitomo Chemical cumene method and the hydrogen peroxide method. In the cumene PO-only process,

oxygen and hydrogen are required in the oxidation and hydrogenation processes, respectively, but when hydrogen peroxide is synthesized by the anthraquinone method in the hydrogen peroxide method, oxygen and hydrogen are used, and when the process is considered with the inclusion of the hydrogen peroxide synthesis process, there is no difference in the secondary raw materials that necessary. The most important point in the hydrogen peroxide process is how inexpensively one can produce hydrogen peroxide, which is used in large quantities. Furthermore, in terms of problems with the process, there is the necessity of carrying out a slurry reaction because the drop in activity of the epoxidation catalyst (TS-1) is rapid. Also, dilution with an organic solvent such a methanol is necessary to obtain a sufficient epoxidation reaction rate, and therefore, it can be assumed that a large

amount of energy will be required for separating out the water produced and recovering and recycling the methanol solvent.[17], [18]

Conclusion

In this paper we gave an explanation of existing PO production methods and an overview of the cumene PO-only process newly developed by Sumitomo Chemical. The Sumitomo Chemical PO-only production technology reached the stage of plant production in the short time of four years from the laboratory stage, but we would like to add that in this development, we implemented strict and earnest concurrent engineering with the manufacturing team starting in the initial stages. Three years have passed since the plant start-up, and the fact that during this time operations have gone favorably is also the fruit of our collaboration. We would like to put effort into increasing the performance of catalysts and improving processes to make leaps and bounds with this process as a truly global technology.

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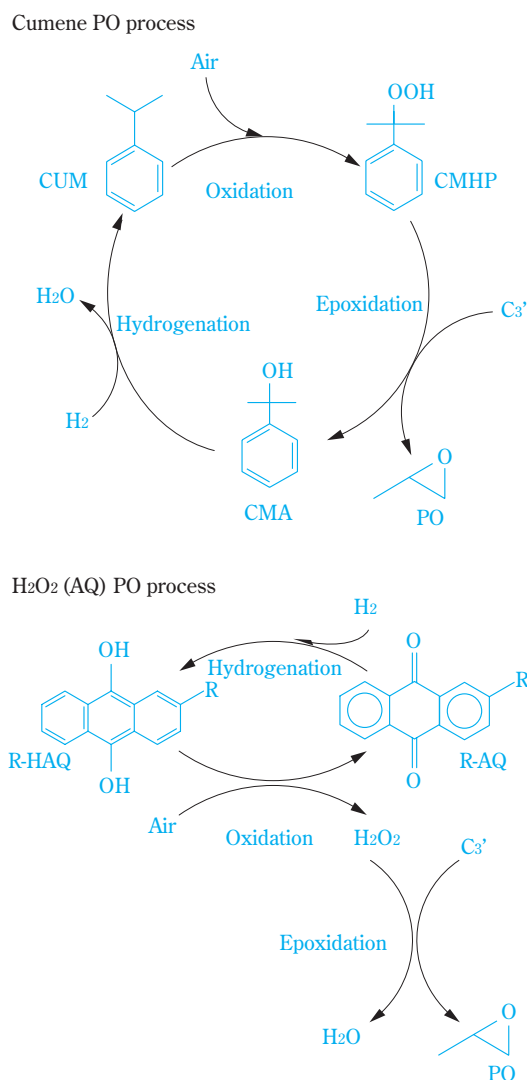15) S. T. Oyama, K. Murata, M. Haruta, Catalysts & Catalysis, **46**, 13 (2004).

Cumene PO process

H₂O₂ (AQ) PO process

Fig. 9 Comparison of PO production process between Cumene route and Hydrogen peroxide (H₂O₂) route (AQ : Anthraquinone)

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