Introduction

Propylene oxide (PO) is a major industrial product with a production of more than 7 million tons per year worldwide. Approximately 70% of it is used as polypropylene glycol, a raw material for urethane, and the remainder is used as propylene glycol, a raw material for unsaturated polyesters, food product additives, and cosmetics. The demand for urethane is growing remarkably, particularly in Asia, and one PO producer after another is announcing business plans for new plants.

The industrialized PO production methods developed to date are summarized here. There are three main production methods: the PO-only production method using chlorine, the co-production method that produces co-products such as styrene monomer (SM) along with the PO, and the PO-only production method operated by Sumitomo Chemical.

Among these processes, the PO/SM co-production method is important because styrene monomer is the raw material for polystyrene (PS) with a production of over 25 million tons per year worldwide. Polystyrene is the fourth most widely produced polymer following polyethylene, polypropylene, and polyvinyl chloride. In the future, particularly in Asia, the demand for polypropylene glycol and PS are expected to increase significantly.

After briefly reviewing the current industrial processes for producing PO, this paper introduces the features of a new acetophenone hydrogenation process developed by Sumitomo Chemical in the PO/SM co-production method.

Existing PO production processes

The existing production methods mentioned above are briefly reviewed below. Further details can be found in the literature.

1. Chlorine method

Propylene and chlorine are reacted to produce a mixture of α- and β-chlorohydrin (9:1); next, PO is synthesized by reaction with an alkali compound (e.g., calcium hydroxide).
2. Organic peroxide method

(1) PO-only production method

Sumitomo Chemical has developed a PO-only production method using cumene hydroperoxide (CMHP). Cumene is oxidized in air to obtain cumene hydroperoxide. Cumylalcohol (CMA) and PO are obtained from CMHP and propylene in the presence of a high activity Ti epoxidation catalyst. CMA is hydrogenated to obtain cumene, which is recycled in the process.

(2) Co-production method

The organic peroxide method was first developed by Halcon Corp. and Atlantic Richfield Oil Corp. (later ARCO) in the 1970s. In a method using ethylbenzene, the indirect epoxidation of propylene using ethylbenzene hydroperoxide (EBHP) as the organic peroxide produces PO. Styrene monomer (SM) is obtained as the co-product. Major producers using PO/SM co-production are LyondellBasell Industries and Shell Chemicals Ltd., but in Japan, only Nihon Oxirane Co., Ltd., produces PO using this co-production method. Reflecting the recent trends in demand for the two co-products, new PO plants have exclusively employed the PO/SM co-production method. Described below is the PO/SM co-production process in more detail.

First, the air oxidation of ethylbenzene produces ethylbenzene hydroperoxide, and acetophenone is co-produced as a by-product. Next, ethylbenzene hydroperoxide and propylene are reacted in the presence of an epoxidation catalyst, and α-phenyl ethanol and PO are produced. The α-phenyl ethanol produced undergoes a dehydration reaction in the presence of an acid catalyst to form SM. Mo-based homogeneous catalysts or Ti supported silica based heterogeneous catalysts are often used as the epoxidation catalyst.

These organic peroxide methods use the oxidative power of hydroperoxides effectively and have the advantage of not requiring a secondary raw material such as chlorine. With the ethylbenzene method, approximately 2.5 tons of styrene is co-produced for every ton of PO.

Existing PO/SM Process by the EBHP method

Figure 1 shows the existing PO/SM process (SRI Consulting). This process is constructed in sections.

1) Oxidation section in which ethylbenzene (EB) is oxidized by air to obtain ethylbenzene hydroperoxide (EBHP), accompanied by acetophenone (ACP) as a by-product.

2) Epoxidation section in which α-phenyl ethanol (αPE) and PO are obtained from EBHP and propylene in the presence of an epoxidation catalyst.

3) Dehydration distillation section in which αPE, containing ACP, is dehydrated and SM is obtained.

4) Hydrogenation section in which the ACP, separated by distillation, is hydrogenated to obtain αPE, which is recycled back to the dehydration section.

5) PO purification section wherein PO is purified.
In the processes of both companies, improvement of EB consumption is realized by producing αPE through the hydrogenation reaction of by-produced ACP under a high pressure condition (8.4MPa, SRI Consulting) and by recycling this αPE to the dehydration section.

As mentioned above, in the PO/SM process, 5-10% ACP is produced as a by-product in the oxidation section, and some is produced in the epoxidation section.

**Improvement in the competitive power of the PO/SM plant at Sumitomo Chemical Co., Ltd.**

1. Development of a new ACP hydrogenation catalyst

Problematically, the existing processes had required high pressure hydrogen for ACP hydrogenation and large quantities of hydrogen in excess of ACP. In addition, in the hydrogenation reaction, a sufficient yield had not been achieved due to by-products such as EB. In order to solve these problems, Sumitomo Chemical attempted to develop a new catalyst with high activity and high selectivity.8)

(1) Improvement of catalyst activity

Researchers have found that copper system catalysts such as CuO-ZnO (SRI Consulting7) and CuO-Cr2O3 9) could be used as an ACP hydrogenation catalyst. Figure 2 shows the ACP hydrogenation scheme using noble metal catalysts. In the case of hydrogenation using a Pd-carbon catalyst, αPE is first produced, followed by the successive production of EB. In particular, αPE readily undergoes hydrogenolysis with an acid. Selective production of αPE using a Pd catalyst is thought to be difficult. In the case of using a Rh-carbon catalyst, αPE is first produced as in the case of a Pd catalyst, followed by the successive production of cyclohexyl ethanol.10), 11)

As mentioned above, when using supported noble metal catalysts, the hydrogenation of benzene nuclei and the hydrogenolysis of hydroxyl groups occurs. Because of these processes, catalysts with copper systems are used to keep the quantities of the by-products low.

Although copper catalysts have long been used as hydrogenation catalysts, they tend to sinter easily. Therefore, copper catalysts have been made fit for practical use by preparing mixed oxides with compounds such as ZnO and Cr2O3, to improve their thermal stabilities. Compared to other metals, copper has a significant tendency to sinter and to be easily reduced by hydrogen (see Table 1).12)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Pd, Pt, Rh, Ru</th>
<th>Ni</th>
<th>Cu</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction Temperature/°C</td>
<td>room temp.</td>
<td>350</td>
<td>180</td>
<td>450</td>
</tr>
</tbody>
</table>

Today, from the point of view of human health and the environment, the trend is to develop chromium-free catalysts. We have also investigated the copper system catalyst based on CuO-SiO2 in order to develop a high activity ACP hydrogenation catalyst. As basic compounds, for example CeO2 and MgO, have been known to prevent sintering of copper catalysts.13) We have also investigated SiO2 carrier and basic compounds in order to prevent catalyst sintering.

Table 2 shows compares two CuO-SiO2 catalysts, one treated with a specific basic compound and the other not treated. The hydrogenation activities per 1 g of the catalyst were compared by the examination of the ACP hydrogenation reaction using an autoclave. Table 2 shows that an improvement of more than two-fold for the catalytic activity on adding the specific basic compound. Moreover, the effect was apparent even with a very small addition.

The new treatment of the CuO-SiO2 catalyst with a basic compound was effective in preventing copper sintering, similar to the addition of ZnO or Cr2O3.
A recent study on the treatment of CuO-SiO₂ catalysts with basic compounds (see Fig. 3) showed that the peak temperature for temperature programmed reduction (TPR) shifted from 256°C to 335°C with the increase in content of basic compounds in the catalyst, from (1) to (5). Based on this report, we speculated that for low temperature reduction, our CuO-SiO₂ catalyst treated by the specific basic compound was reduced slower than the untreated catalyst. This characterization indirectly showed that our catalyst tolerated sintering.

(2) Improvement of catalyst selectivity

As already described above, ACP hydrogenation uses a catalyst that does not hydrogenate benzene nuclei. Moreover, when the catalyst is acidic, EB is produced by hydrogenolysis at the benzyl position (see Equation 1). EB is produced as a by-product of hydrogenolysis of αPE (see Equation 2). In order to produce αPE from ACP in high selectivity, the development of a non-acidic copper catalyst is required.
Table 3 shows that the amount of EB decreased significantly by treating the catalyst with the specific basic compound. Also, Table 3 indicates that the new catalyst showed a higher activity because the mass flow rate when using the new CuO-SiO₂ catalyst was twice that of the conventional CuO-Cr₂O₃ catalyst. We attributed the improvement of catalytic activity to both the preparation method of the catalyst, as explained so far, and to the molding method of the catalyst pellet. Although the molding of copper catalysts has been considered to be very difficult for a long time now,¹⁸–²⁰ the development of a new simple and strong molded catalyst that is tolerant to a liquid phase fixed bed flow system was achieved by the improvement of the binder and the molding method.

2. Development of the new process

We performed a bench scale test by using the new molded catalyst synthesized at the laboratory in order to evaluate its performance in the large scale. A fixed bed flow system with two tubes of 1 m was used for a life test of 1 year. By using the apparatus, we collected engineering data of the reaction in the gas, liquid, and solid phases, and real-scale equipment was designed by scale-up methods. As shown in Fig. 5, the rate constant representing the catalyst activity exhibited initial deactivation for 1000 h and showed mild deactivation after 1000 h. Even then, the ACP conversion was maintained at about 95% for 8000 h, and the catalyst life was thought to have achieved a satisfactory level. Moreover, hydrogenated product was confirmed to not contain any impurities that might affect the subsequent section.

The improvement of the catalytic activity due to the new catalyst resulted in decreasing the operation pressure and realizing compact production equipment. Because the new hydrogenation process can be operated at 1–3 MPa, compared to the old process operated at around 8.4 Mpa, and (1) because the surplus hydrogen is not needed for ACP hydrogenation, neither a high pressure compressor for hydrogen gas nor (2) a high pressure compressor for recycling hydrogen gas is required. Because of these reasons, we have developed a new process (see Fig. 6) with a low process energy cost that is also environment-friendly.

![Fig. 5](image5.png)

**Table 3** Comparison of EB by-product between Conventional Cat. and New Cat. of hydrogenation

<table>
<thead>
<tr>
<th></th>
<th>Conventional Cat. CuO-Cr₂O₃</th>
<th>New Cat. CuO-SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACP Conversion (%)</td>
<td>84.0</td>
<td>89.2</td>
</tr>
<tr>
<td>mass flow ratio</td>
<td>1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>αPE Selectivity (%)</td>
<td>94.1</td>
<td>99.9</td>
</tr>
<tr>
<td>EB Selectivity (%)</td>
<td>2.9</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Experimental conditions : 180°C, 2.4MPa, Pellet, catalyst reduction : 180°C

Next, from the point of view of equipment cost, (1) the high pressure compressor is not needed, as mentioned above. Moreover, because of the development of the new pre-reduction method for the catalyst, where the catalyst is reduced in the liquid phase instead of the ordinal vapor phase, (2) the equipment for hot hydrogen supply is not needed. By using the newly developed reduction method, sintering of the catalyst in the liquid phase is decreased because heat transfer between the catalyst and liquid is good. Moreover, because the continuous phase in the new hydrogenation reactor is the liquid phase whereas that of the old hydrogenation reactor was the gas phase, a small amount of catalyst can now accomplish the hydro-

![Fig. 6](image6.png)

Sumitomo ACP hydrogenation process
genation reaction with enough residence time. (3) The above factors make the hydrogenation equipment compact. By implementing the above improvements, we were able to build a new PO/SM process where the low operation pressure and high yields lead to a reduction in energy costs and equipment costs, making the process very competitive.

3. Competitive power of the new PO/SM process in the world

The new ACP hydrogenation process developed by Sumitomo Chemical was licensed to Nihon Oxirane Co., Ltd., and was put into practice in 1998. The competitive power of the PO/SM process was improved by the new hydrogenation technology at Nihon Oxirane Co., Ltd. Moreover, the company succeeded in expanding the production capacity by implementing new technology, which contributed to an increase in profits. The new process is still running smoothly today at this company. The new ACP hydrogenation process developed by Sumitomo Chemical has been licensed overseas, owing to its strong competitiveness. In the future, as more PO/SM plants are built, we will continue to license this new technology.

Because we have already developed several technologies for the PO/SM process, the new hydrogenation process of ACP also forms a part of the overall process development. The new hydrogenation technology will contribute significantly to the PO/SM business of Sumitomo Chemical and related companies.

Conclusion

Sumitomo Chemical’s new acetophenone hydrogenation technology was developed within only one year of bench-scale evaluation. Despite the 10,000 times scale-up of mass flow from bench-scale apparatus to real-scale equipment, the target result was accomplished as planned with the real-scale equipment. This result emphasizes the high quality of engineers involved in the commercialization of this process. In the future, in order to maintain this world-class technology, we will continue putting our efforts into enhancing the ACP hydrogenation technology.

Finally, the authors thank JGC Catalyst & Chemicals Ltd. for collaborative research on the development of the catalyst.

References

13) BASF, WO2005058853 (2005)
Development of a New Acetophenone Hydrogenation Process for Propylene Oxide Production

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