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Propylene epoxidation over titanium-on-silica catalyst—the heart of the SMPO process

J.K.F. Buijink*, J.J.M. van Vlaanderen, M. Crocker, F.G.M. Niele

Shell International Chemicals, Shell Research and Technology Centre Amsterdam, P.O. Box 38000, 1030 BN Amsterdam, The Netherlands

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Abstract

Shell Chemicals operates the styrene monomer propylene oxide (SMPO) process in four world-scale plants and is currently building a fifth plant in China. The heart of this process comprises the epoxidation reaction of propylene with ethyl benzene hydro peroxide to propylene oxide and methyl phenyl carbinol (a styrene monomer precursor) over a proprietary titanium-on-silica epoxidation catalyst. One of the key performance aspects of the SMPO process is the high atom efficiency, partly resulting from the high selectivities in the epoxidation step. The efficiency of the process can be further improved through intimate knowledge of suitable supports for titanium-on-silica catalysts and by gaining increased understanding of the chemistry of catalytic epoxidation. Research in these areas has provided leads to longer-lived, more selective titanium-on-silica catalysts. This is an example of how improvements of the SMPO process support our initiatives in sustainable development.

Keywords: Propylene oxide; China; Hydroperoxidation process; Epoxidation; Titanium-on-silica catalyst; Efficiency improvements; Catalyst support; Mechanism; Sustainable development

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1. Introduction

World current PO production is approximately 6 million metric tons per year. Two technologies dominate the production: hydroperoxidation (practiced in various forms by Lyondell, Shell, Sumitomo and Repsol) and chlorohydrin (Dow).

Shell Chemicals operates the styrene monomer propylene oxide (SMPO) process since 1979. Following recent expansions (partly in joint ventures), four world-scale plants have a combined installed capacity of over 870 kt of propylene oxide (PO) and 1900 kt of styrene (SM) per annum. The plants are located close to market in The Netherlands and Singapore. The multi-step process based on hydroperoxidation uses a number of catalysts, the most important of which is a proprietary titanium-on-silica epoxidation catalyst [1].

The heart of the SMPO process comprises the epoxidation reaction of propylene with ethyl benzene hydro peroxide (EBHP) to propylene oxide and methyl phenyl carbinol (MPC) over titanium-on-silica catalyst. After separation, the latter is converted to styrene by catalytic dehydration over alumina. The EBHP feed for the epoxidation step is prepared by air oxidation of ethyl benzene (EB), which is in turn prepared by alkylation of benzene with ethylene, catalysed by a zeolite. A graphic representation of the main SMPO process reactions can be found in Scheme 1.

One of the key performance aspects of the SMPO process is the high atom efficiency. Rewriting the main chemical reactions in one for propylene oxide formation and one for styrene formation illustrates this:

$$\text{Propylene} + [\text{O}] \rightarrow \text{PO}$$

$$\text{Ethyl benzene} + [\text{O}] \rightarrow \text{SM} + \text{H}_2\text{O}$$

For making PO and SM only oxygen is needed, which can conveniently be taken from air. The O–O bond of activated oxygen, in the form of the hydro peroxide, is split efficiently by the titanium-on-silica catalyst, thus making epoxidation the key catalytic step in the process. The chemical selectivities for this step (EBHP-to-PO, EBHP-to-MPC and propylene-to-PO) are between 95 and 98%. Nevertheless, it is realised that a further increase of selectivity can lead to less waste, reduced energy consumption and lower costs. The latter is also true for an increase of the effective lifetime of the catalyst.

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* Corresponding author.
E-mail address: jan-karel.buijink@shell.com (J.K.F. Buijink).

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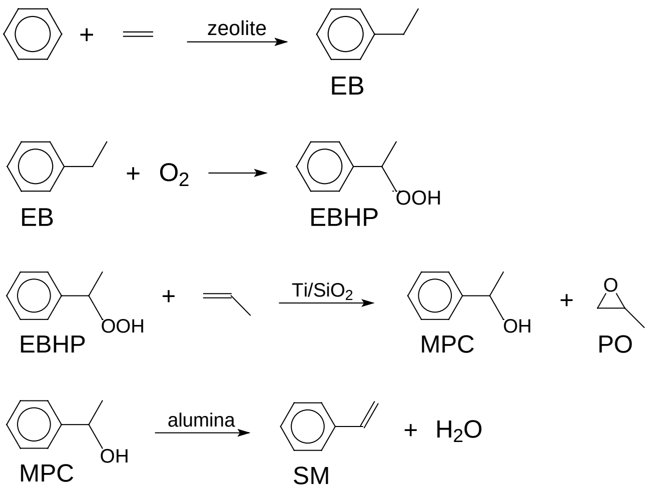

Scheme 1. SMPO process reactions.

The next SMPO expansion will be realised in China, where a world-scale SMPO plant will become part of a new chemical complex in Nanhai, a joint venture with China National Offshore Oil Corporation (CNOOC) and Guangdong Province. To support this new plant and the existing ones, further catalyst improvements are sought through increased understanding of the chemistry of epoxidation and intimate knowledge of suitable supports for titanium-on-silica catalysts. For the latter, we have set up research cooperations with both material suppliers and selected academic researchers. In line with our principles of sustainable development [2], we plan to do so in China as well.

Here we will discuss recent developments in epoxidation catalyst research as well as some aspects of our growing understanding of the epoxidation reaction.

2. Experimental

2.1. Materials and substances

The silica gel carrier used in the experiments had a surface area of 300 m^2/g and a weight average particle size of about 1 mm, unless indicated otherwise. Substantially all particles had a particle size between 0.6 and 1.4 mm.

Titanium tetrachloride, hexamethyldisilazane and tetra-(isopropyl) titanate were obtained from Aldrich and used as received. Titanium isopropoxy heptacyclopentyl silsesquioxane and tetrakis(trimethylsilyl)titanate were made according to EP0876360.

In the extrusion experiments the following ingredients are used:

HP321	Particulate silica powder ex Crossfield
SIPERNAT 50	Particulate silica powder ex Degussa (SIPERNAT is a trademark)
MEOA	Mono-ethanol amine
SUPERFLOC N100	Flocculation agent (SUPERFLOC is a trademark)
NALCO 7879	Flocculation agent (NALCO is a trademark)
PVA	Polyvinylalcohol

2.2. Synthesis and manipulation of supports

2.2.1. Support 1

In this experiment silica extrudates are prepared. The ingredients used in their respective amounts were:

SIPERNAT 50 (g)	2867
NALCO 7879 (g)	100
MEOA (g)	125
Water (g)	5550
Additional water (g)	250

All silica powder was charged into a mixer/muller and the mixing and kneading was started. After 1 min a solution of MEOA in water was added. After 35, 50 and 60 min respectively 125, 50 and 75 g of additional water were added. After 90 min the flocculation agent NALCO 7879 was added. After 95 min the mixing and kneading stopped. The resulting plastic pieces were subsequently extruded.

Extrusion took place in a 2.25 in. Bonnot extruder provided with a dieplate of a 1.3 mm trilobe. The screw speed in the extruder was 20 rpm (rotations per minute).

The extrudates thus obtained were dried for 2 h at 120 °C and subsequently the temperature was raised to 800 °C over a period of 3 h, at which temperature the extrudates were maintained for 2 h. After cooling the extrudate strings were broken and sieved resulting in trilobes with a diameter of 1.3 mm and a length/diameter ratio of about 3.

The extrudates were subsequently soaked in water for 1 h, filtered and dried for 2 h at 120 °C. The properties of the extrudates are listed in Table 1.

Table 1
Properties of supports

	Support 1	Support 2	Support 3	Silica gel (G57 ex-Grace)
Flat plate strength (N/cm)	55	58	71	–
Surface area (m^2/g, Hg)	263	257	411	300
Pore volume (ml/g, Hg)	1.27	1.21	1.06	1.05

2.2.2. Support 2

The steps for support 1 were repeated except that the wet extrudate was passed into a spheroniser after passing through a 0.8 mm cylindrical dieplate. In the spheroniser spheres having a diameter of 1.4 mm were formed. These spheres were subsequently dried and calcined (Table 1).

2.2.3. Support 3

The ingredients used in their respective amounts to prepare the silica extrudates were:

HP321 (g)	169
NALCO 7879 (g)	5
SUPERFLOC N100 (g)	4.5
MEOA (g)	6
PVA, 5% in water (g)	61
Water (g)	256

All silica powder was charged into a mixer/muller and the mixing and kneading was started. After 3 min SUPERFLOC was added and after 13 min a solution of MEOA and PVA in water was added. After 40 min of mixing and kneading the powdery mix changed into a mix consisting of plastic pieces and to these plastic pieces NALCO was added. After 44 min an extrudable mixture was discharged.

Extrusion took place in a 1 in. Bonnot extruder provided with a dieplate of a 0.8 mm trilobe. The screw speed in the extruder was 30 rpm.

The extrudates thus obtained were dried for 2 h at 120 °C and subsequently the temperature was raised to 550 °C over a period of 2 h, at which temperature the extrudates were maintained for 2 h. After cooling the extrudate strings were broken and sieved resulting in trilobes with a diameter of 0.8 mm and a length/diameter ratio of about 3.

The extrudates were subsequently soaked in water for 1 h, filtered and dried for 16 h at 120 °C. The properties of the extrudates are listed in Table 1.

2.2.4. Support 4

Used titania-on-silica catalyst spheres (2 mm diameter) were subjected to a decoking treatment at 450–500 °C for approximately 5 h (air). Subsequently 150 g of the decoked catalyst spheres were washed two times with 500 ml of an aqueous 1.0 M ammonium nitrate solution (i.e. liquid/solid ratio of about 5/1) by adding the spheres to the ammonium nitrate solution and gently stirring the solution at room temperature for 90 min. The washed decoked catalyst spheres were then filtered and washed two times with 200 ml distilled water on a Buchner funnel. This procedure of washing with ammonium nitrate and water was repeated once. The resulting spheres were dried in air at 120 °C for 2 h. Finally, the spheres were calcined in air for 2 h at 300 °C. After the treatment, essentially only crystalline titania phases (35.6% anatase, 62.4% rutile) could be found by XRD.

2.3. Catalyst preparation

All supports listed above were used to prepare titanium-on-silica catalysts according to the general procedure listed below, yielding catalysts 1–4, respectively.

Seventy grams of the appropriate support were loaded into a quartz reactor tube and heated to 260 °C under a nitrogen flow of 73 Nl/h. The support was kept at 260 °C for 2 h. Hereafter the support was cooled to 195 °C and 15 g gaseous titanium tetrachloride ($TiCl_4$) was passed through the support bed over a period of 70 min while a nitrogen flow of 5 Nl/h was maintained as well. After termination of the $TiCl_4$ distillation, dry nitrogen was led over the support bed for 2 h at 195 °C and at a rate of 5 Nl/h. The impregnated support was then heated in a nitrogen atmosphere to 600 °C (at a rate of 50 °C/h) and calcined for 6 h at 600 °C. The calcined silica/titania catalyst was cooled to 325 °C, while the nitrogen flow was increased to 10 Nl/h. Then steam was added to the nitrogen circulating over the catalyst. Steam treatment was thus carried out by passing steam over the catalyst bed at a rate of 4 g/h for 2 h at 325 °C. The reactor was subsequently cooled to 200 °C in a stream of dry nitrogen. Hexamethyldisilazane was then passed over the catalyst bed at a rate of 18 g/h for 2 h using dry nitrogen as a carrier gas (at a rate of 5 Nl/h). An exotherm of 30 °C was observed, indicating a reaction of hexamethyldisilazane with hydroxyl groups in the catalyst. Excess of hexamethyldisilazane was stripped with nitrogen (75 Nl/h).

2.4. Catalyst characterization

The elemental composition of the catalysts was determined by X-ray fluorescence for Ti and by flash combustion for C. Anatase and rutile loadings were determined quantitatively using XRD. The amount of X-ray amorphous titania in the catalysts was calculated by subtracting of the measured amounts of rutile and anatase from the total amount of titania according to elemental analysis. Solid state MAS NMR spectra were recorded at 300 MHz (^1H).

2.5. Epoxidation experiments

The epoxidation experiments were carried out in a continuous epoxidation bench scale unit containing two vessels on automatic weight balances containing respectively the EBHP and alkene feed streams, two high pressure pumps, a fixed bed reactor, a third pump for pumping a recycle stream over the reactor, means to maintain the reactor continuously at temperatures between 60 and 120 °C, a stripper to remove light boiling components like propene, a cooler and a vessel for receiving the product.

The feeds were supplied to the reactor via the two high pressure pumps and mixed together before entering the reactor. The reactor was operated liquid full at 40 bar pressure. A large recycle stream was maintained over the reactor to have isothermal operation of the reactor bed and to ensure that the catalyst to be re-activated is contacted with epoxidation reaction product. The feed of propene and a 35 wt.% EBHP solution in ethyl benzene was mixed with the recycle stream prior to introduction into the reactor.

A compositional analysis of the reaction mixture was carried out by means of super critical fluid chromatography (SFC).

The following process conditions were maintained:

Throughput EBHP solution	30 g/h
Throughput propene	18 g/h
Recycle flow	2.5 kg/h

The activity of the catalyst is expressed as "K85" indicating the reaction rate constant in kg^2 of liquid per kg of catalyst per mole per hour ($kg^2/(kg\,mol\,h)$) normalised at 85 °C assuming that first order reaction kinetics apply in EBHP and in propene. The K85 is determined as the mean K85 over 300 h of operation at 90 °C.

The selectivity of the catalyst is calculated as the mean selectivity to propene over a period of 300 h at 90 °C.

The epoxidation experiment above was used to test catalyst 1, catalyst 2, catalyst 3, a catalyst on silica gel (G57 ex-Grace), catalyst 4 and a catalyst on fresh silica spheres.

For the dosing experiments a modified continuous propylene epoxidation experiment was performed. After starting up the continuous epoxidation bench scale unit with a partially deactivated catalyst ex-commercial operation, the unit was operated under the conditions indicated at a temperature of 110 °C and without titanium dosing until a certain conversion level was reached at which the reaction rate remained at a constant level for about 50 h (approximately from runhour 100 to runhour 150). The reaction rate expressed as K85 was about 3.0 $kg^2/(kg\,mol\,h)$.

Then, after approximately 150 runhour, the dosing of titanium was started. The soluble titanium compound was added as a 0.05 wt.% stock solution in dry ethyl benzene to the reaction mixture prior to introduction into the reactor. In all experiments the titanium compound was dosed in such amount that the titanium level in the reaction mixture was 10 ppmw calculated as metallic Ti and based on total reaction mixture.

3. Results and discussion

3.1. Improving the epoxidation catalyst

The epoxidation catalyst used in the SMPO process consists of dispersed titanium-on-silica [1]. It is made in-house by a unique gas-phase process comprising:

1. impregnating a silicium compound with a stream of gaseous titanium tetrachloride diluted with nitrogen,
2. calcining the obtained reaction product of step 1,
3. hydrolysis of the product of step 2,
4. silylation of the product of step 3.

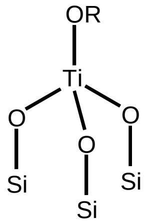

Fig. 1. Key active species of titanium-on-silica catalyst (Si denotes silicium compound, R is $SiMe_3$ when hexamethyldisilazane is used as a silylating agent).

During the first two steps, it is thought that three Ti–Cl bonds of titanium tetrachloride are sequentially replaced by Ti–O–silica bonds by reaction of titanium chloride with surface silanol groups on the silicium compound, under the elimination of HCl. In step 3, the remaining chloride on the catalyst is removed by hydrolysis of the calcined product. Finally, the resulting Ti–OH bonds, and the remaining surface silanol groups are contacted with a silylating agent to reduce surface acidity and hydrophilicity by converting them to silyl ether bonds. A very suitable silylating agent is hexamethyldisilazane. All steps of the catalyst preparation can conveniently be performed in a single reactor. A graphic representation of what is believed to be the key active species of this heterogeneous epoxidation catalyst can be found in Fig. 1.

S. Hauka et al. have performed elegant studies in which they developed an adequate description of the chemistry involved in treatment of silica surfaces with titanium tetrachloride and hexamethyldisilazane [3]. In addition, we were able to show on the silylated titanium-on-silica catalyst the presence of distinct OR (R = SiMe3) groups on titanium centers by solid state ^{29}Si CP MAS NMR ($\delta = 17.2$ ppm TiOSiMe3, $\delta = 14$ ppm SiOSiMe3).

Catalyst research has concentrated on optimising the support as well as on optimising the recipe for making titanium-on-silica catalysts. Ideally, the support should be chemically inert, yet allow easy grafting of the titanium via gas phase impregnation. In addition, it should have high porosity as well as sufficient mechanical stability. Silica gel meets these requirements well, and has therefore been the preferred support at the start of the process. However, later work has shown that other silica sources, such as precipitated or fumed silica and even silica gel fines can be used to make silica extrudates [4]. These extrudates allow more control of properties at all length scales and can have high mechanical stability (see Table 1). They often outperform silica gel as a support for titanium-on-silica catalysts (see Table 2). For a large part, these improvements are thought to be correlated to changes in the pore structure and surface properties of the extrudates with respect to silica gel.

Table 2
Epoxidation results for catalysts on various supports

	Catalyst 1	Catalyst 2	Catalyst 3	Catalyst on silica gel (G57 ex-Grace)
K85 ($kg^2/(kg\,mol\,h)$)	18.8	20.0	34.9	14
Selectivity (wt.%)	95.0	95.2	95.3	90.4
Ti weight (%)	5.59	2.19	3.7	3.7
C weight (%)	3.2	2.12	3.1	3.0
Rutile weight (%)	6.5	1.0	1.4	1.9
Anatase weight (%)	0.2	0.9	0.9	0.5
Amorphous TiO_2 (wt.%)	2.6	1.7	3.8	3.9

Other methods of changing the properties of silica gel have been explored, such as changing silica surface properties by calcination. The opportunities to change the pore structure of silica gel during and after synthesis are somewhat limited.

Apart from increasing the lifetime of the catalyst by optimising support and performance of the catalyst, there is also the option of re-using spent catalyst. A simple sequence of decoking, washing with an aqueous mineral acid solution and calcination of the resulting material turns a spent titanium-on-silica catalyst into a support material again, thus diminishing the amount of inorganic waste from the SMPO process [5].

Interestingly, there is significant increase in selectivity due to this treatment without loss of activity.

3.2. Improving propylene epoxidation

The titanium-on-silica catalyst shows considerable deactivation, while maintaining high selectivity for prolonged times. The activity loss can empirically be related to: (1) leaching of titanium, (2) restructuring of the titanium phase and (3) fouling of the catalyst by organic residues. Epoxidation research has concentrated on increasing the lifetime of titanium-on-silica catalysts by on-line reactivation, and on elucidating the mechanism of epoxidation. Reactivation of (partly) deactivated titanium-on-silica catalyst is possible by the addition of soluble titanium compounds to the feed of the epoxidation step [6]. The results are displayed in Table 3. Upon addition of low amounts of titanium complexes, the activity of the entire catalyst bed was found to double. The activity of these compounds as homogeneous epoxidation catalysts is negligible under the reaction conditions. We believe that only when covalently attached to the silica surface, i.e. when they become heterogeneous, these compounds are active catalysts.

Table 3
Activation of partly deactivated titanium-on-silica catalyst with various soluble titanium complexes

	Hours of addition				
	0	20	40	60	80
K85 for complex 1	3.0	4.7	6.0	6.6	6.6
K85 for complex 2	3.0	4.6	6.0	6.0	6.0
K85 for complex 3	3.2	6.3	6.1	5.9	5.9

Complex 1 is titanium isopropoxy heptacyclopentyl silsesquioxane, complex 2 is tetrakis(trimethylsilyl)titanate, complex 3 is tetra(isopropyl) titanate.

For the epoxidation of propylene with organic hydro peroxide by titanium-on-silica catalysts, we suggest the simplified mechanism depicted in Fig. 2. In essence, this mechanism is a modified version of the so-called Sharpless-type mechanism: one coordination site on titanium is occupied by an η_2-peroxo ligand, formed by reaction of a coordinatively unsaturated titanate complex with an organic hydro peroxide. The activated, distal oxygen of the η_2-peroxo ligand is directly attacked by the olefinic bond of propylene, yielding PO and a titanium alkoxide. The titanium alkoxide is protolysed by the next hydro peroxide, thus closing the catalytic cycle. One of the intriguing aspects of this mechanism is the necessity of a ‘proton parking place’ on the active site. After ‘proton parking’ the Ti–O–Si moieties are seriously weakened, which opens up a pathway to titanium leaching via further peroxolysis. Loss of titanium bonded to silica does not only lead to loss of activity, but can also influence selectivity by the formation of Brønsted-acidic silanol groups. To find further supporting evidence for this mechanism, we have a research cooperation with Prof. J.M. Basset at the Centre National de la Recherche Scientifique in Lyon, France. Basset et al. have shown to be capable of creating and derivatising discrete tripodal titanium hydrides on a silica surface via surface organometallic chemistry [7], and are

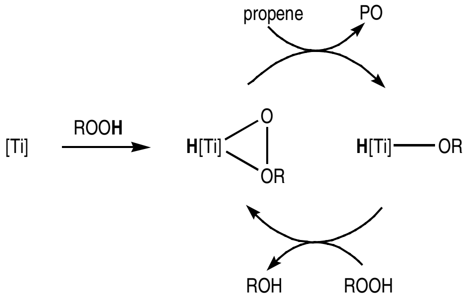

Fig. 2. Simplified catalytic cycle for propene epoxidation with hydro peroxides. [Ti] denotes a coordinatively unsaturated titanate site.

currently studying their reactivity in propylene epoxidation with organic hydro peroxides.

4. Conclusion

The SMPO process is an efficient way of making two chemical commodities, PO and SM. The heart of the process is formed by the catalytic epoxidation of propylene over a heterogeneous titanium-on-silica catalyst. The efficiency of the process can be further improved through intimate knowledge of suitable supports for the epoxidation catalyst and by gaining increased understanding of the chemistry of catalytic epoxidation. Research in these areas has provided leads to longer-lived, more selective titanium-on-silica catalysts. This is an example of how improvements of the SMPO process support our initiatives in sustainable development.

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