# Trends and Views in the Development of Technologies for Chlorine Production from Hydrogen Chloride

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Sumitomo Chemical Co., Ltd. has developed a catalytic process that is highly recognized and applied worldwide as a technology for recycling the hydrogen chloride generated as by-product in isocyanate plants into chlorine. In this article we outline the trends and views in the development of various technologies for chlorine production from hydrogen chloride, and present the recent advances in catalyst technology for the Sumitomo Chemical process.

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## Introduction

Chlorine ($Cl_2$) is used as a starting material for products such as polyvinyl chloride monomers, isocyanates (such as TDI and MDI), epichlorohydrin and various fluorocarbons. However, for example in the case of toluene diisocyanate (TDI), which is manufactured according to the following formulas (1) and (2), 4 moles of hydrogen chloride (HCl) are produced as a byproduct for each 1 mole of TDI.

$$CO + Cl_2 \rightarrow COCl_2 \tag{1}$$

$$CH_3C_6H_3(NH_2)_2 + 2COCl_2 \rightarrow CH_3C_6H_3(NCO)_2 + 4HCl \tag{2}$$

Approximately half of the 42 million tons of $Cl_2$ produced annually is estimated to end up as HCl by-product generated in the way described above, or as various other chlorides.[1)]

Normally, the HCl produced as a byproduct is directly sold as 35% aqueous hydrochloric acid or used as the starting material for oxychlorination of vinyl chloride monomers, while surplus amounts are disposed of using methods such as neutralization treatments. However, the expansion in demand for vinyl chloride monomers is smaller than that for isocyanates, and in the future we can expect that the excess of HCl will increase further.

In addition, $Cl_2$, which is a starting material, is normally produced by salt electrolysis, but since the expansion of the demand for chlorine is greater than that of the demand for the caustic soda (NaOH) produced along with it, there is a danger that the demand balance between $Cl_2$ and NaOH will collapse.

Under these circumstances, technology for converting the HCl produced as a byproduct to $Cl_2$ and reusing it not only helps in effective use of excess HCl, but is also helpful to balance the salt electrolysis. Since, in turn, this leads to conservation of resources and energy, it has been studied for 100 years.

In this article, we report on trends in the processes for producing chlorine from HCl and also introduce new, improved technology for the Sumitomo Chemical HCl oxidation process which has been licensed to several companies in Japan and overseas.

## Method for Producing Chlorine from HCl and Its Features

Methods for producing $Cl_2$ from HCl are roughly divided in three; electrolysis processes, oxidizing agent recirculation processes, and catalytic oxidation.

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## 1. Electrolysis process for aqueous hydrochloric acid

This method is called the Uhde process, and since its commercialization in the 1960s it is being operated in multiple plants throughout the world.[2)] The HCl starting material is absorbed in water, and after the formation of a 22% aqueous solution of hydrochloric acid, it is sent to the anode and cathode. $Cl_2$ is obtained from the anode and $H_2$ from the cathode. The conversion ratio for HCl is 20%, and the 17% aqueous hydrochloric acid from the electrolyzer is recycled to the electrolysis process after adjusting its concentration. The HCl and water present in the $Cl_2$ gas generated at the anode are separated, obtaining the $Cl_2$ product.

In terms of the trends in the development of this technology, Bayer, UhdeNora (joint venture between Uhde and DeNora) and DeNora have jointly developed a technology that can reduce power consumption by approximately 30% by using an oxygen depolarized cathode (ODC), which in turn reduces the electrolysis voltage.[3)] **Fig. 1** shows a schematic diagram of an electrolysis vessel, and **Fig. 2** presents a comparison of the electrolysis voltage with the conventional method.

After operating a 20,000 ton per year demonstration plant at its Brunsbüttel plant in Germany in 2003, Bayer started operating a commercial plant capable of producing 215,000 tons of chlorine per year at a TDI and MDI plant at the Shanghai Industrial Park in 2008.

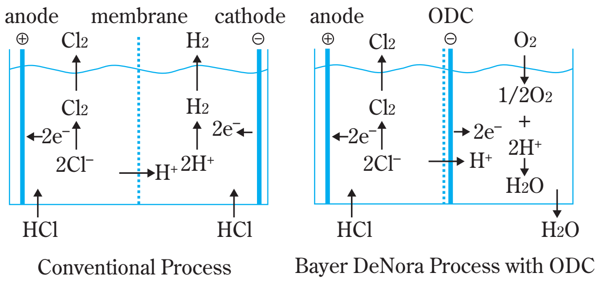

**Fig. 1** Comparison of HCl electrolysis

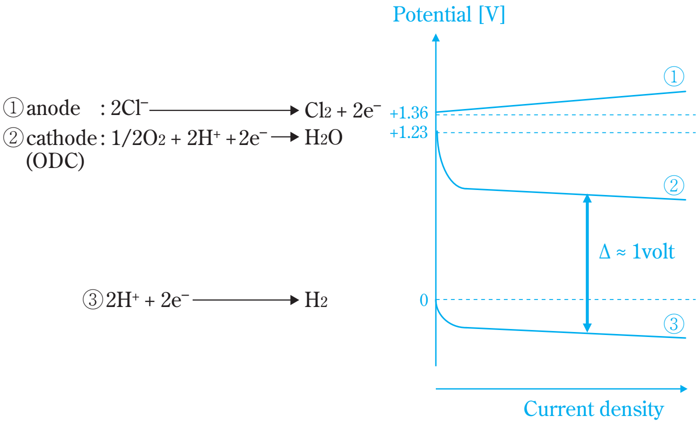

**Fig. 2** Electrode potentials in HCl electrolysis

## 2. HCl gas electrolysis process

The DuPont process makes use of a Nafion ion exchange membrane and is known as a HCl gas electrolysis process.[4)] An ion exchange membrane covered with a porous catalyst containing noble metals such as Pt and Ru is used for the electrolysis membrane, and HCl gas supplied to the anode chamber is oxidized by the surface of the anode, producing chlorine gas. The generated protons ($H^+$) pass through an ion exchange membrane, then reach the cathode to be reduced to $H_2$. Dilute hydrochloric acid is supplied to the cathode to control the wetness and temperature of the membrane. The HCl conversion ratio is 70–85%, but since the HCl is reacted as a gas, there is the advantage of the HCl absorption process being unnecessary. After the $Cl_2$ and HCl gases that are obtained are dried with sulfuric acid, the $Cl_2$, HCl and inert gases are separated and product $Cl_2$ is obtained. The unreacted HCl is recycled to the electrolysis process. Evaluations were carried out in the 1990s using a demonstration plant, but there has been no report of its industrialization.

While technical improvements are being made to the aqueous hydrochloric acid and HCl gas electrolysis processes described above, the large amount of electric power that is consumed is still a problem.

## 3. Oxidizing agent circulation methods

The Kel-Chlor process developed by Kellogg can be mentioned, having as its main features the use of nitrogen oxides as the catalyst and sulfuric acid as the circulation medium.[5)] The elementary reactions are shown in equations (3)–(7), and the complete reaction is shown in equation (8).

$$2HCl + 2NOHSO_4 \rightarrow 2NOCl + 2H_2SO_4 \tag{3}$$

$$2NOCl \rightarrow 2NO + Cl_2 \tag{4}$$

$$2NO + O_2 \rightarrow 2NO_2 \tag{5}$$

$$NO_2 + 2HCl \rightarrow NO + Cl_2 + H_2O \tag{6}$$

$$NO + NO_2 + 2H_2SO_4 \rightarrow 2NOHSO_4 + H_2O \tag{7}$$

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$$4HCl + O_2 \rightarrow 2Cl_2 + 2H_2O \tag{8}$$

Since the process is complicated and there is much equipment that uses expensive materials, construction costs are high; therefore, it is said to be suitable for large-scale plants that can benefit from economy of scale. DuPont started operation of a 200,000 ton per year plant in 1974, but it is not operating at present.

### 4. Catalytic oxidation of HCl gas

Since the discovery of the Deacon process[6] using a $CuCl_2$ catalyst in 1868, there have been many reports of improved catalysts and articles on processes for catalytic oxidation. Reaction equation (9) shows the reaction for producing chlorine using catalytic oxidation, with no side reactions.

$$2HCl + \frac{1}{2}O_2 \overset{\text{catalyst}}{\rightleftarrows} Cl_2 + H_2O + 59kJ/mol \qquad (9)$$

Using a copper chloride-potassium chloride-rare earth compound/$SiO_2$ catalyst, which was an improvement on the Deacon catalyst, Shell developed a fluidized bed air oxidation process capable of reactions at lower temperatures in 1960.[7] This catalyst system achieves a high catalytic performance by using $CuCl_2$ to which alkali metal chloride and a rare earth chloride are added, generating a molten salt in reaction conditions. A 30,000 ton per year commercial production facility was operated in the 1970s, but it is said that it was stopped shortly thereafter.

Mitsui Toatsu Chemicals, Inc. (currently Mitsui Chemicals, Inc.) developed the MT-Chlor process, which is a fluidized bed process for oxidation with pure oxygen that uses a $Cr_2O_3 \cdot SiO_2$ catalyst. In 1988 Mitsui Toatsu Chemicals made it commercially viable at its Omuta plant, and is currently commercially operating at 60,000 tons per year.

Under the conditions of the reaction, the catalyst operates without melting, and the reaction takes place using only the oxidation-reduction reaction without going through the chloride-oxide reaction cycle of the Deacon system. Therefore, the chromia active species maintains its state as an oxide and the stability of the catalyst is greatly improved. The reaction temperature in the fluidized bed reactor is 350 to 400°C, and the conversion rate for HCl is 75% or more in one pass.[8]

Though not reaching commercial viability, Mortensen et al. have reported a two-stage fluidized bed system that uses a Deacon catalyst.[9] A flow scheme is shown in **Fig. 3**. In the first reactor (oxidizer), CuCl is oxidized at 360 to 400°C in the presence of HCl and oxygen, obtaining $Cl_2$ and CuO. This CuO is fed to the second reactor (chlorinator), and CuCl produced by absorbing/reacting the unreacted HCl on the CuO at a relatively low temperature of 180 to 200°C. $Cl_2$ is obtained with about 100% yield by circulating the catalyst through both fluidized beds.

Among these catalytic oxidation methods, the MT-Chlor process, which was discovered in Japan, and the Sumitomo Chemical process, which will be described in the following, are the processes that are currently being operated commercially.

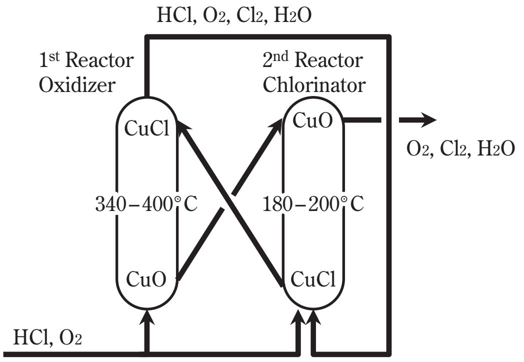

**Fig. 3** Scheme of circulating dual fluidized-bed reactor

## The Sumitomo Chemical Chlorine Production Process

Aiming at an environmentally friendly process, Sumitomo Chemical developed a fixed bed process, which as a catalytic oxidation method, uses a $RuO_2$/rutile-type $TiO_2$ catalyst.[10]

Since the $RuO_2/TiO_2$ (rutile) catalyst has a higher activity than conventional catalysts and a sufficient reaction rate can be obtained even at low temperatures (**Fig. 4**) that are superior in terms of equilibrium for the

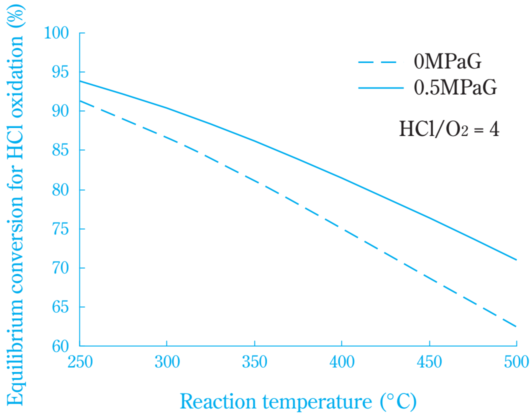

**Fig. 4** Equilibrium conversion curves for HCl oxidation reaction as a function of reaction temperature

reaction in equation (9), the conversion ratio is high. In addition, as it has a high thermal stability as a main feature, it makes possible a long-term continuous operation of the fixed bed reactor.

### 1. Use of highly active $RuO_2/TiO_2$ (rutile) catalyst

The Sumitomo Chemical process uses a highly active, long life $RuO_2/TiO_2$ (rutile) catalyst. Research on catalysts for $O_2$ oxidation of HCl has mainly focused on the field of base metals such as Cu, Cr, Fe, Mn and Ni. Only Shell[11] has reported investigations on the use of noble metals, but those catalysts were obtained by building up the results of investigations focusing on the reactivity of the outermost d electrons of noble metals such as Pt, Rh, Ir, Ru and Os. **Fig. 5** shows the results of screening for catalysts, but the Ru metal catalysts showed specific activity as noble metal catalysts. Increased activity of approximately 50 times that of conventional catalysts was observed by changing the active species from metallic Ru to $RuO_2$ and the $TiO_2$ carrier to the rutile phase.

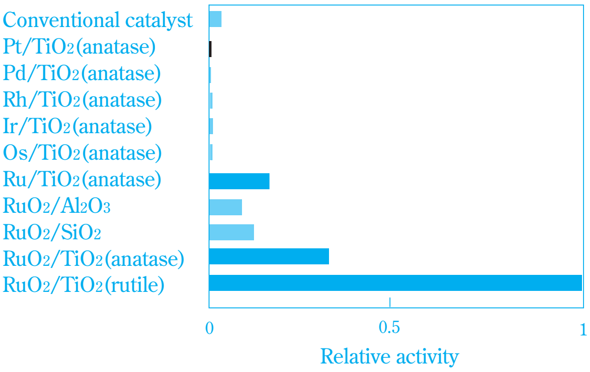

**Fig. 5** Relative activities of the HCl oxidation catalysts

(1) Structure of $RuO_2/TiO_2$ (rutile) catalyst

The $RuO_2/TiO_2$ (rutile) catalyst has a unique structure in which $RuO_2$ crystallites with a size of 0.3 × 0.9 nm cover the surface of the rutile titania.

**Fig. 6** shows a TEM image of the $RuO_2/TiO_2$ catalyst. With $RuO_2$ on anatase $TiO_2$, $RuO_2$ particles on a nanometer order similar to that of normal supported catalyst are observed (**Fig. 6** (a)), but with $RuO_2$ on rutile $TiO_2$, they are not (**Fig. 6** (b)).

Furthermore, when the $RuO_2/TiO_2$ (rutile) catalyst was studied by FE-STEM, a thin $RuO_2$ layer of nanometer order could be found supported on the $TiO_2$ primary particle surface as in **Fig. 7**.

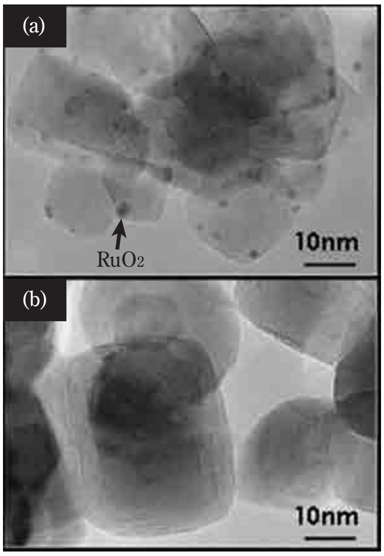

**Fig. 6** TEM images of $RuO_2/TiO_2$ catalysts[12]
(a) $RuO_2$/anatase-$TiO_2$ catalyst
(b) $RuO_2$/rutile-$TiO_2$ catalyst

**Fig. 7** FE-STEM image of $RuO_2$/rutile-$TiO_2$ catalyst[12]

The crystallite size of this thin layer of $RuO_2$ was analyzed from the EXAFS Fourier transform spectrum. As shown in **Fig. 8**, $RuO_2$ has a rutile structure, and one Ru atom is surrounded by 2 nearest neighbor Ru atoms (atomic distance = 0.31 nm, hereinafter abbreviated to Ru-Ru1), 8 next nearest neighbor Ru atoms (atomic distance = 0.35 nm, hereinafter abbreviated to Ru-R2) and 6 O atoms (atomic distance = 0.19 nm [2 atoms], 0.20 nm [4 atoms], hereinafter abbreviated to Ru-O). **Fig. 9** shows the Fourier transform spectrum for $RuO_2/TiO_2$ (rutile), and peaks belonging to Ru-R1, Ru-R2 and Ru-O can be found. The intensity of these peaks is a lower intensity than a standard $RuO_2$ sample with a sufficiently large crystallite. The coordination number for Ru in $RuO_2$ is low, suggesting that $RuO_2$ is present in very fine crystals. Analyzing the EXAFS oscillation, we found the coordination numbers for Ru-Ru1 and Ru-Ru2 and carried out a simulation that approximated a rectangular solid with the a and b axes vertical and horizontal, and the c-axis as the height. By combining the

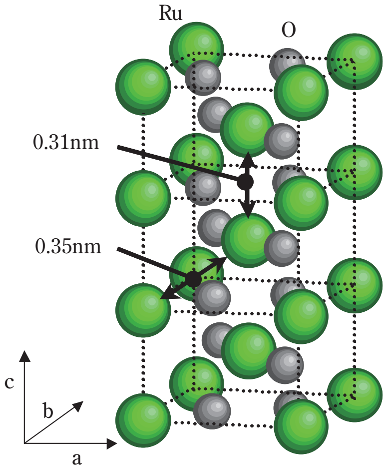

**Fig. 8** Ball model showing a bulk $RuO_2$ crystal[12)]

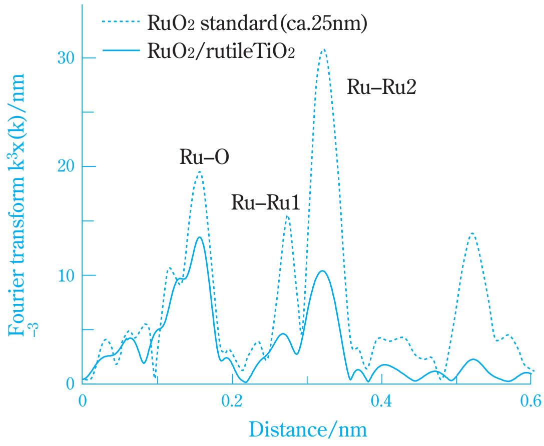

**Fig. 9** Fourier transforms of the EXAFS spectra of (a) $RuO_2$ standard and (b) $RuO_2$/rutile-$TiO_2$ catalyst[12)]

coordination numbers obtained, we estimated the size of the $RuO_2$ crystallite to be 0.3 × 0.9 nm.

From the results of FE-STEM and EXAFS analysis, we concluded that the $RuO_2/TiO_2$ (rutile) catalyst has a structure in which ultra-fine crystallites of $RuO_2$ with dimensions of approximately 0.3 × 0.9 nm cover the surface of the rutile $TiO_2$ primary particles, as in **Fig. 10**. This 0.3 nm corresponds to the thickness of one unit cell of the $RuO_2$ crystallite. Putting it another way, $RuO_2$ crystallite covered an estimated 90% of the $TiO_2$ surface from the relationship between the specific surface area for $TiO_2$ and the support quantity of $RuO_2$.

(2) Industrial catalyst

This catalyst provides both the catalytic activity and life to satisfy the performance needs of an industrial catalyst. The main reason it shows a high level of catalytic activity is the high level of dispersion of the $RuO_2$ due to the specific structure of the $RuO_2$ and the rutile $TiO_2$. In addition, the high thermal stability can be thought of as being due to the strong interaction between $RuO_2$ and $TiO_2$.

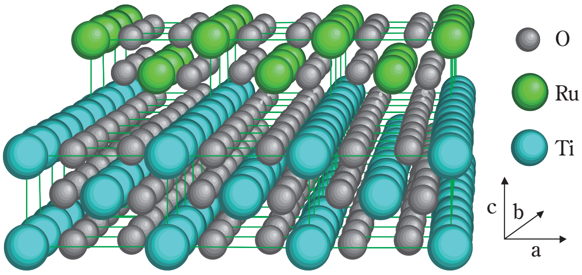

**Fig. 10** Ball model of $RuO_2$/rutile $TiO_2$ catalyst surface[12)]

The strong interaction between metallic Ru and $TiO_2$ has been thoroughly reported[13)], but the interaction between $RuO_2$ and $TiO_2$ has also been described[14)]. According to the latter, when a complex oxide of $RuO_2$ and $TiO_2$ is formed, the sublimation of the Ru component in the high-temperature reaction is limited to 1/40 of corresponding non-supported $RuO_2$.

In addition to improve the activity and thermal stability of the catalyst as discussed above, an industrial catalyst for a fixed bed reactor high thermal conductivity is required in order to efficiently eliminate the reaction heat generated in the oxidation reaction of HCl and pure $O_2$. Therefore, in the development of the industrial catalyst, we were able to increase the thermal conductivity of the catalyst up to approximately 1.5 times that of the catalyst initially developed by making various improvements in its physical properties.

## 2. Overview of the process

One key feature of the Sumitomo Chemical process is achieving a compact fixed bed reactor by developing a highly active, long-life catalyst. In this way it is possible to produce $Cl_2$ with a higher purity than electrolysis of salt, in high yields, at low cost. An example of the process is shown in **Fig. 11**.

(1) Oxidation reaction step

HCl and oxygen are supplied to a multitubular fixed bed reactor, and $Cl_2$ and water are obtained by a gas phase reaction using the $RuO_2/TiO_2$ (rutile) catalyst.

To use the entire catalyst layer effectively, the reactor is divided into multiple zones, then controlling the temperature independently in each zone. On the shell side of each zone, heat transfer salt (HTS) is circulated to

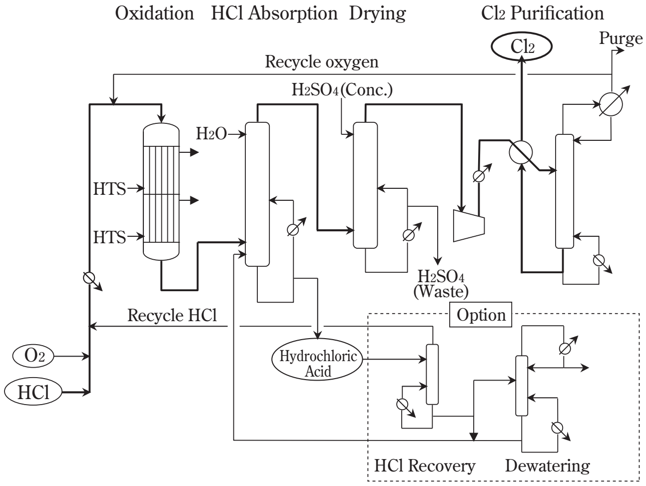

**Fig. 11** An example of HCl oxidation process flow[12)]

eliminate the reaction heat, making it possible to adjust to the target reaction temperature. The eliminated heat is recovered as steam by a heat recovery boiler and is used effectively in the process.

(2) HCl absorption step

The reaction gas is quenched, and the unreacted HCl is absorbed in water and separated from the bottom of the column as hydrochloric acid. The gas obtained at the top of the column, which is mainly composed of $Cl_2$ and $O_2$, is next sent to a drying step.

Since the previous oxidation reaction is carried out at a comparatively low temperature, the hydrochloric acid obtained from the bottom of the column is not contaminated by sublimation of the catalyst component. It may easily be commercialized as hydrochloric acid produced as a byproduct.

When higher $Cl_2$ yields would be desired, HCl can be separated from the hydrochloric acid by distillation at increased pressure, and then recycled to the reaction. For cases in which further increased $Cl_2$ yields would be required, the liquid from the distillation column is supplied to a dewatering column, distilled in a vacuum and only water is removed at the top of the column. By returning the liquid in the column to the process, it is possible to recover almost all feed HCl as $Cl_2$.[15)]

(3) Drying step

The water containing gas obtained in the HCl absorption process is supplied to a drying column, and it is dried by bringing it into contact with concentrated sulfuric acid. Sulfuric acid that contains water is obtained from the bottom of the column.

(4) Chlorine purification step

The $Cl_2$ is liquefied by compressing and cooling the dry gas from the drying step, which contains $Cl_2$, $O_2$ and inert components. Furthermore, highly pure $Cl_2$ is obtained by distilling and eliminating the impurities present in the solution. Most of the uncondensed gas containing $O_2$ is recycled to the reaction process, and to prevent accumulation of substances such as inert components, part of it is purged to a caustic scrubber.

## 3. Demonstration of catalyst performance and process

The 1000 ton per year demonstration plant shown in **Fig. 12** was constructed, and the performance of the $RuO_2/TiO_2$ (rutile) catalyst and overall process was confirmed.

**Fig. 12** HCl oxidation demonstration pilot plant[12)]

As shown in **Fig. 13**, it was possible to maintain the HCl conversion ratio at the targeted 85% for two years of demonstration operations, and there were no problems with respect to corrosion resistance and durability of the equipment and materials or with operability.

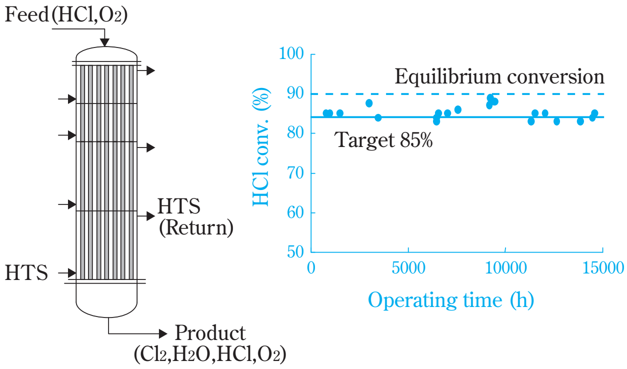

**Fig. 13** HCl conversion as a function of time in operation in the demonstration reactor[12)]

**Fig. 14** shows an FE-STEM Z contrast image of the catalyst used for two years. It can be seen that the thickness of the $RuO_2$ crystal layer exposed to the $TiO_2$ carrier surface increased because of sintering. We can presume that this $RuO_2$ sintering is related to deactivation of the catalyst, but the catalyst life reached the target without trouble. Furthermore, the $Cl_2$ obtained from the demonstration plant had higher purity than chlorine from electrolysis as shown in **Table 1**.

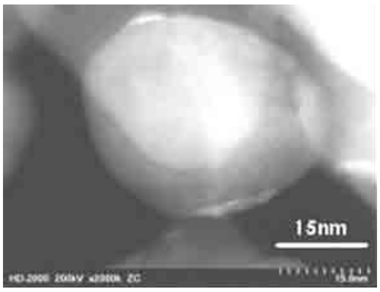

**Fig. 14** FE-STEM image of the used catalyst after two years of operation 12)

**Table 1** Comparison of the quality of chlorine obtained by Sumitomo HCl oxidation and by electrolysis of sodium chloride 12)

| Component | Sumitomo HCl oxidation (%) | Electrolysis (%) |
|---|---|---|
| $Cl_2$ | 99.90 | 99.1 |
| $O_2$ | 0.08 | 0.6 |
| $N_2$ | 0.01 | 0.2 |
| $H_2$ | N.D. | 0.1 |

After the demonstration of this technology, it was licensed amongst others to a domestic chemical producer in 2002, starting operation of around 100,000 tons per year that continues its operation to the present day, and has since then been licensed to several companies in Japan and overseas.

## 4. Catalyst improvement technology

(1) Development Concept

Typically, we can consider the following three cases for the sintering of supported metals: 1) The case where the crystallites themselves migrate on the carrier collide and aggregate; 2) the case where the atoms in the crystals move on the carrier and are absorbed by other crystallites; 3) the case where the constituents in the crystals vaporize and are again absorbed by other crystallites.16) – 18) Considering the fact that the $RuO_2$ and $TiO_2$ in this catalyst system have a strong interaction and a high level of thermal stability as was discussed previously, we assumed that the sintering mechanism was two-dimensional as in the above 1) and 2).

Therefore, we thought that we might be able to control the $RuO_2$ sintering by adding particles of a size having the same particle diameter as the $RuO_2$ on the carrier surface as in **Fig. 15**.

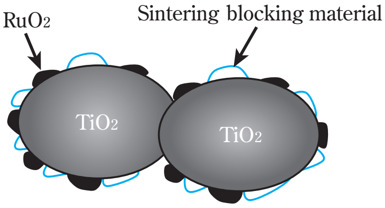

**Fig. 15** Conceptual model of the preventing $RuO_2$ of sintering on the $RuO_2/TiO_2$ catalyst surface

(2) Development of improved catalyst

Several examples have been reported on adding a third component to a catalyst for the purpose of preventing sintering. For example, for preventing the sintering of the carrier, there are the methods of adding $La_2O_3$ and $CeO_2$ to $\gamma$-$Al_2O_3$19), 20) and stabilized zirconia21) that adds Y to $ZrO_2$. Others methods prevent sintering by highly dispersing the active species, as for example co-impregnation of a mixed aqueous solution of Zr, Hf and Ti compounds and $RuCl_3$ 22), or the method of adding $CeO_2$ and MgO to a $Pd/Al_2O_3$ catalyst to prevent Pd sintering.20), 23)

Since highly corrosive gas is present in the oxidation reaction for HCl, the sintering blocking material must be carefully selected taking into account the chemical stability and thermal stability in the reaction atmosphere. In addition, the sintering blocking material must be supported at a nanometer level to control nano-order $RuO_2$ sintering.

As a result of examining various types of blocking additives and addition methods, we found that a catalyst where nano-order $SiO_2$ and $RuO_2$ were supported on the $TiO_2$ surface showed a strong effect in sintering prevention. **Fig. 16** shows a SEM image of (a) the $TiO_2$ surface, (b) $RuO_2/SiO_2/TiO_2$ catalyst and (c) image (b) after 5 minutes of exposure to an electron beam. Roughness can be seen on the $TiO_2$ surface in (b) while the $TiO_2$ surface presents a smooth image as shown in (a).

The $RuO_2$ is reduced if it is exposed to an electron beam for 5 minutes in the field of view in (b), and it can be seen that nano-order metallic Ru particles appeared in between the bumps of the rough surface.

From these results, we could presume that the roughness seen in the image in (b) is seen mainly as $SiO_2$, and $RuO_2$ is present in the spaces in between, corresponding to a catalyst very close to the concept model in **Fig. 15**.

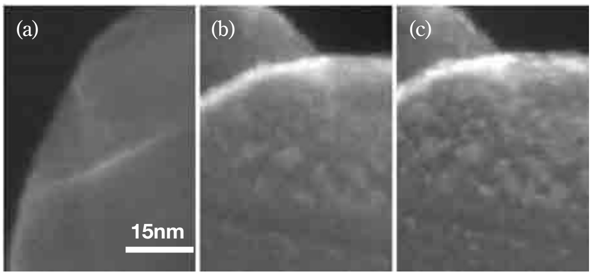

**Fig. 16** SEM images of catalyst surface[12]
(a) $TiO_2$ surface
(b) $RuO_2/SiO_2/TiO_2$ surface
(c) $RuO_2/SiO_2/TiO_2$ surface after irradiation of electrons for 5 minutes

(3) Evaluation of the improved catalyst thermal stability

**Fig. 17** shows the changes over time in the $RuO_2$ crystallite with the same spatial velocity and same conversion conditions when the reaction of HCl and $O_2$ was carried out with and without the addition of $SiO_2$. Since it was difficult to observe the $RuO_2$ in this catalyst system with an electron microscope, we analyzed the EXAFS Fourier transform spectrum and calculated the crystallite diameter. The $RuO_2$ crystallite diameter was the same with or without the addition of $SiO_2$ before the reaction, but the system with the added $SiO_2$ ($RuO_2/SiO_2/TiO_2$) had a stable $RuO_2$ crystallite diameter for 1000 hours after the start of the reaction, confirming that the nano-order crystallite diameter was maintained.

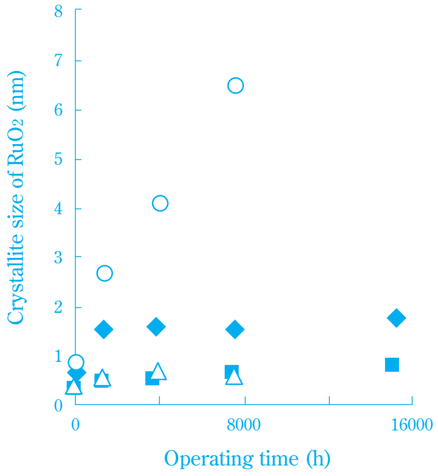

**Fig. 17** $RuO_2$ crystallite size as a function of time in operation under HCl oxidation reaction[12]
$RuO_2/TiO_2$ (○; a,b-axes, △; c-axis),
$RuO_2/SiO_2/TiO_2$ (◆; a,b-axes, ■; c-axis).

Considering the fact that the sintering prevention effect was found with this reaction system with the $SiO_2$ on the same order as the $RuO_2$, we can assume that the sintering mechanism is mainly the migration of the crystallites themselves.

The improved catalyst that was developed prevents $RuO_2$ sintering and maintains a high level of activity; thus allowing us to reduce the amount of Ru used, and in addition, opening the possibility for highly competitive catalysts that are not as easily affected by the variations in price typical of noble metals.

## Economics

Sumitomo Chemical has not only been able to carry out continuous operation using the long-life catalyst and highly reliable process for two years, but has also found this process to be superior economically. The reasons are: (1) the catalyst costs are reduced because of the highly active, long-life catalyst; (2) the one-pass conversion ratio is high because of the use of a fixed bed reactor; (3) $Cl_2$ is obtained with a high yield because almost all of the unreacted hydrochloric acid is recovered; (4) the electric power consumption is a fraction of that for electrolysis; (5) the recovery of the reaction heat in steam, makes the process energetically efficient; (6) construction costs are low because the various pieces of equipment, beginning with the reactor, are compact; and high quality $Cl_2$ is obtained.

**Table 2** compares unit consumption of the Sumitomo Chemical process and the Bayer-DeNora process,[24] which is a hydrochloric acid electrolysis process. The Bayer-DeNora process reduces the electricity consumed by about 30% over the conventional electrolysis process by using an oxygen depolarized cathode. Even so, there is a large difference in the unit consumption of electricity, and we can assume that the Sumitomo Chemical process will produce $Cl_2$ at a lower cost, depending on the site conditions. In addition, since the $CO_2$ emissions are low because of the decreased power

**Table 2** Comparison of unit consumption between Sumitomo HCl oxidation method and Bayer-DeNora electrolysis method[12)]

| Unit consumption (Units/T-Chlorine) | Sumitomo HCl oxidation | Bayer-DeNora electrolysis |
|---|---|---|
| HCl (Ton) | 1.05 | 1.03 |
| $O_2$ ($Nm^3$) | 163 | 159 |
| Power (kwh) | 165 | 1100 |

consumption, it is superior in terms of measures against global warming, making it an extremely competitive chlorine production process.

## Conclusion

Recently, there have been several reports giving examples of research on $RuO_2/TiO_2$ (rutile) in a HCl oxidizing atmosphere. According to Crihan et al., it is presumed that the state where the bridging O in $RuO_2$ is substituted with Cl in the HCl oxidation reaction ($RuO_xCl_y$) is a stable activated state.[25)] According to López et al., from density functional theory (DFT) and experimental data, there are steps for which the main points are re-bonding with $Cl_2$ and re-adsorption of $O_2$ after the chlorination of $RuO_2$.[26)] In addition, Zweidinger et al. used in situ surface x-ray diffraction analysis and analyzed the $RuO_2/TiO_2$ in the HCl oxidation atmosphere; as a result, they concluded that the high chemical stability of $RuO_2$ under high-temperature HCl and the gradual sintering activity were factors in the high performance of $RuO_2/TiO_2$.[27)]

The Sumitomo Chemical HCl oxidation technology is highly regarded not only because it makes it possible to recycle the HCl produced as a byproduct, but also as a more resource conserving and energy efficient technology than salt and hydrochloric acid electrolysis technology, with a low impact on the environment. In addition, the plants that have been licensed up to now are operating without problems, and the catalyst and process are highly reliable. In the coming future, we would like to further improve both catalyst and process, and make a worldwide contribution with this as a technology for preventing global warming.

## References

1) S. Motupally, D. T. Mah, F. J. Freire and J. W. Weidner, *Electrochem. Soc. Interface*, **7** (3), 32 (1998).
2) Uhde's brochure, *Chlorine and hydrogen from hydrochloric acid by electrolysis* (1990).
3) Bayer News release, September (2009).
4) E. I. Du Pont de Nemours and Company, US patent 5411641 (1995).
5) A. G. Oblad, *Ind.Eng.Chem.*, **61** (7), 23 (1969).
6) H. Deacon, GB patent 1403 (1868).
7) Shell Oil Company, US patent 3210158 (1965).
8) T. Kiyoura, K. Yoshida and H. Nishida, *Shokubai*, **33** (1), 15 (1991).
9) M. Mortensen, R. G. Minet, T. T. Tsotsis and S. W. Benson, *Chemical Eng. Sci.* **54**, 2131 (1999).
10) K. Iwanaga, K. Seki, T. Hibi, K. Issoh, T. Suzuta, M. Nakada, Y. Mori, T. Abe, *SUMITOMO KAGAKU*, **2004-I,** 1 (2004).
11) Shell International Research Maatschappij, GB patent 1046313 (1966).
12) K. Seki, *Catal. Surv. Asia*, **14**, 168 (2010).
13) S. J. Tauster et al., *J. Am. Chem. Soc.*, **100**, 170 (1978).
14) Johnson Matthey, US Patent 3945948 (1976).
15) Sumitomo Chemical Company Limited, JP patent 4182608 (2008).
16) E. Ruckenstein and B. Pulvermacher, *J. Catal.*, **29**, 224 (1973).
17) P. C. Flynn and S. E. Wanke, *J. Catal.*, **34**, 390 (1974).
18) C. H. Bartholomew, *Appl. Catal. A: General*, **212**, 17 (2001).
19) M. Ozawa and M. Kimura, *J. Mater. Sci. Lett.*, **9** (3), 291 (1990).
20) T. Hayata, T. Furuya, S. Yamanaka and J. Koezuka, *Shokubai,* **31** (2), 116 (1989).
21) W.H. Rhodes, *J. Am.Cer.Soc.,* **64** (1), 19 (1981).
22) Idemitsu Kosan, JP patent, 7-116516 (1995).
23) M. Schmal, A. L. Guimaraes and L. C. Dieguez, *222nd ACS National Meeting*, Chicago, IL, United States, August 26-30, (2001).
24) J. Moorhouse, "Modern chlor-alkali technology, 8", Royal Soc. Chem., Cambridge (2001), p.49.
25) D. Crihan, M. Knapp, S. Zweidinger, E. Lundgren, C. J. Weststrate, J. N. Andersen, A. P. Seitsonen and H. Over, *Angew. Chem. Int. Ed.,* **47**, 2131 (2008).
26) N. López, J. Gómez-Segura, R. P. Marín and J. Pérez- Ramírez, *J. Catal.,* **255**, 29 (2008).
27) S. Zweidinger, J.P. Hofmann, O. Balmes, E. Lundgren and H. Over, *J. Catal.*, **272**, 169 (2010).

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