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# Deactivation factor of $CuCl_2$-KCl/$Al_2O_3$ catalyst for ethylene oxychlorination in a commercial-scale plant

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ABSTRACT

Ethylene oxychlorination over a $CuCl_2$-KCl/$Al_2O_3$ catalyst was examined for 2 consecutive years in a commercial-scale plant. The oxychlorination performance of the $CuCl_2$-KCl/$Al_2O_3$ catalyst deteriorated gradually, which could seriously affect stable operation. To clarify such deactivation factors, the relationship between catalyst performance and physicochemical property change was investigated using X-ray fluorescence, electron probe microanalysis, and Brunauer–Emmett–Teller measurements. Sublimation of the CuCl component and subsequent increment of the ratio of K to Cu components were observed at the inlet of the catalyst bed, and were determined to be contributing factors in the deactivation of the $CuCl_2$-KCl/$Al_2O_3$ catalyst.

## 1. Introduction

The balanced oxychlorination process is the predominant means of manufacturing vinyl chloride monomer (VCM) [1]. The overall process consists of three reactions, as shown in Scheme 1: (1) production of 1,2-dichloroethane (EDC) by direct chlorination of ethylene, (2) production of VCM by thermal decomposition of EDC, and (3) production of EDC by oxychlorination of ethylene using HCl from (2). A significant benefit of oxychlorination is that it recycles hydrogen chloride, which is a by-product in various other reactions, such as the production of diphenylmethanediisocyanate (MDI).

Traditionally, the performance of metal chlorides such as V, Cr, Mn, Fe, Co, Ni, Cu as catalysts for oxychlorination has been studied [2–7]. Thus, in the industrial oxychlorination process, $CuCl_2$ catalysts have traditionally been used owing to their high activity and high selectivity for EDC compared with other transition metal catalysts. For example, it was reported that the reaction result of 99.0% conversion of HCl and 99.6% EDC selectivity was gaved in the catalysts supported 7.98 Cu, 0.78 K and 0.05 Mg as chlorides respectively on alumina ($HCl : C_2H_4 : O_2 = 70.3 : 234.3 : 21.1$ N L/h, the reaction temperature was 493 to 560 K, the amount of catalyst was 303.9 g) [8]. The proposed oxychlorination reaction mechanism with a $CuCl_2$ catalyst is given in Scheme 2. The reaction mechanism has been proposed to progress via ethylene chlorination with $CuCl_2$, followed by reoxidation of the reduced CuCl with $O_2$ and HCl [3,6,3–7,9–12]. However, copper chloride undergoes a redox cycle during this process, which might influence its catalytic performance. Kominami et al. investigated the rates of the chlorination of ethylene and the reoxidation of copper chloride by feeding ethylene gas or a mixed gas of hydrogen chloride and oxygen as pulses to various metal catalysts [6]. They revealed a correlation between the activity of the oxychlorination catalyst and the rate of EDC formation, obtained from the rates of ethylene chlorination and copper chloride reoxidation. Therefore, the oxidation state of Cu is a particularly important parameter.

The oxychlorination of ethylene is an exothermic reaction with high thermal energy ($\Delta H^{\circ} = -239$ kJ/mol) [13]. Various heat removal techniques can be applied to reduce the heat of industrial processes involving exothermic reactions; for example, a heat-exchange reactor can be adopted [14]. Nevertheless, if heat removal is insufficient, partial heat generation occurs in the catalyst layer, which deactivates the Cu-based chloride catalyst. In a patent [15], it has been mentioned that hotspots can reduce the selectivity of the reaction and lead to carbonization of the organic reactants inside the catalyst pellets. Consequently, the pellets can break down into fine powder, and this increases resistance to gas flow along the tube and reduces the life of the catalyst. Therefore, various methods of improving the catalyst durability have been reported, such as the addition of alkali metal chlorides and/or alkaline earth metal chlorides [11,16–26]. However, the durability of Cu-based oxychlorination catalysts is still unsatisfactory in commercial plants. Therefore, it is imperative to investigate the catalyst

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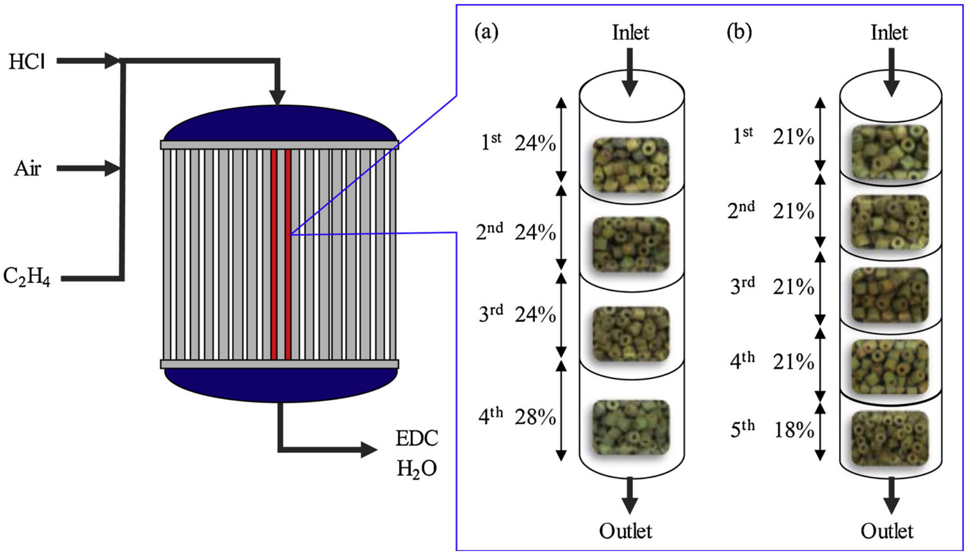


**Scheme 1.** Balanced oxychlorination process.

deterioration state by operation of the industrial plant from the viewpoint of improving industrial catalysts and optimizing the method of their application. In particular, it is important to understand the progression of catalyst degradation at each position of the reactor in order to improve the dilution pattern of the catalyst and extend its life. Nevertheless, there are only a few examples of detailed analysis of the deactivation of the catalyst in industrial operation. Vetrivel et al. analyzed the Cu species of the deactivated catalyst [27,28], by investigating the change in catalyst composition by X-ray photoelectron spectrometry. However, there is no information about the number of runs a spent catalyst can be subjected to. Further, neither the deterioration of the catalyst over time in a plant operation, nor the correlation between the activity and composition at each reactor position was considered.

In this study, using $CuCl_2$-KCl/$Al_2O_3$ catalyst samples taken from actual plant equipment, deterioration factors were estimated from the correlation between the physicochemical analysis (component, surface area, element distribution, etc.) and the activity after long-term operation.

## 2. Experimental method

### 2.1. Catalyst preparation

The $CuCl_2$-KCl/$Al_2O_3$ catalyst was prepared by impregnating γ-alumina (extruded cylinder, outer diameter: 5.0 mm, inner diameter: 2.0 mm, length: 5.0 mm, surface area 184 $m^2 g^{-1}$, pore volume 0.62 mL $g^{-1}$) with aqueous solutions of copper chloride (224 g/L; Nihon Kagaku Sangyo Co., Ltd) and potassium chloride (136 g/L; Otsuka Chemical Co., Ltd). After impregnation, the catalyst was dried at 423 K for 2 h, followed by calcination at 523 K (heating rate: 283 K/min) for 5 h in air using a muffle furnace. Quantitative analysis of copper chloride and potassium chloride was carried out using a scanning X-ray fluorescence analyzer (Rigaku Corporation, (trade name) ZSX PrimusII). About 3 g of the catalyst was pulverized, and then, a sample plate was prepared using a pressure press; subsequently, this plate was subjected to measurements in a Rh tube at a tube voltage of 50 kV and a tube current of 60 mA. The surface area and pore volume were measured using the $N_2$ adsorption method (Microtrac bell BELSORP mini) at liquid-nitrogen temperature and a nitrogen relative pressure of 0.001 to 0.995. Prior to the measurements, the samples (0.1–0.2 g) were weighed and vacuum-dried at 473 K for 4 h. The resultant 13.1 wt% $CuCl_2$–4.9 wt% KCl/$Al_2O_3$ catalyst had a surface area of 112 $m^2 g^{-1}$ and a pore volume of 0.30 mL $g^{-1}$.

### 2.2. Commercial plant test

The prepared catalyst was subjected to an endurance test in a commercial plant reactor set up to renew the catalyst in a two-years. The test catalyst was loaded into the central tube of the reactor consisting of several thousand multi-tubes. The other tubes were filled with a commercial catalyst having a life of 2 years. It was subjected to commercial operation under a flow of reactant gas, and samples were extracted from the reaction tube after 1 and 2 years. The samples were divided into four or five sections, labeled from the inlet side of the reaction tube as 1st, 2nd, 3rd, 4th, or 5th position (Fig. 1).

### 2.3. Activity test

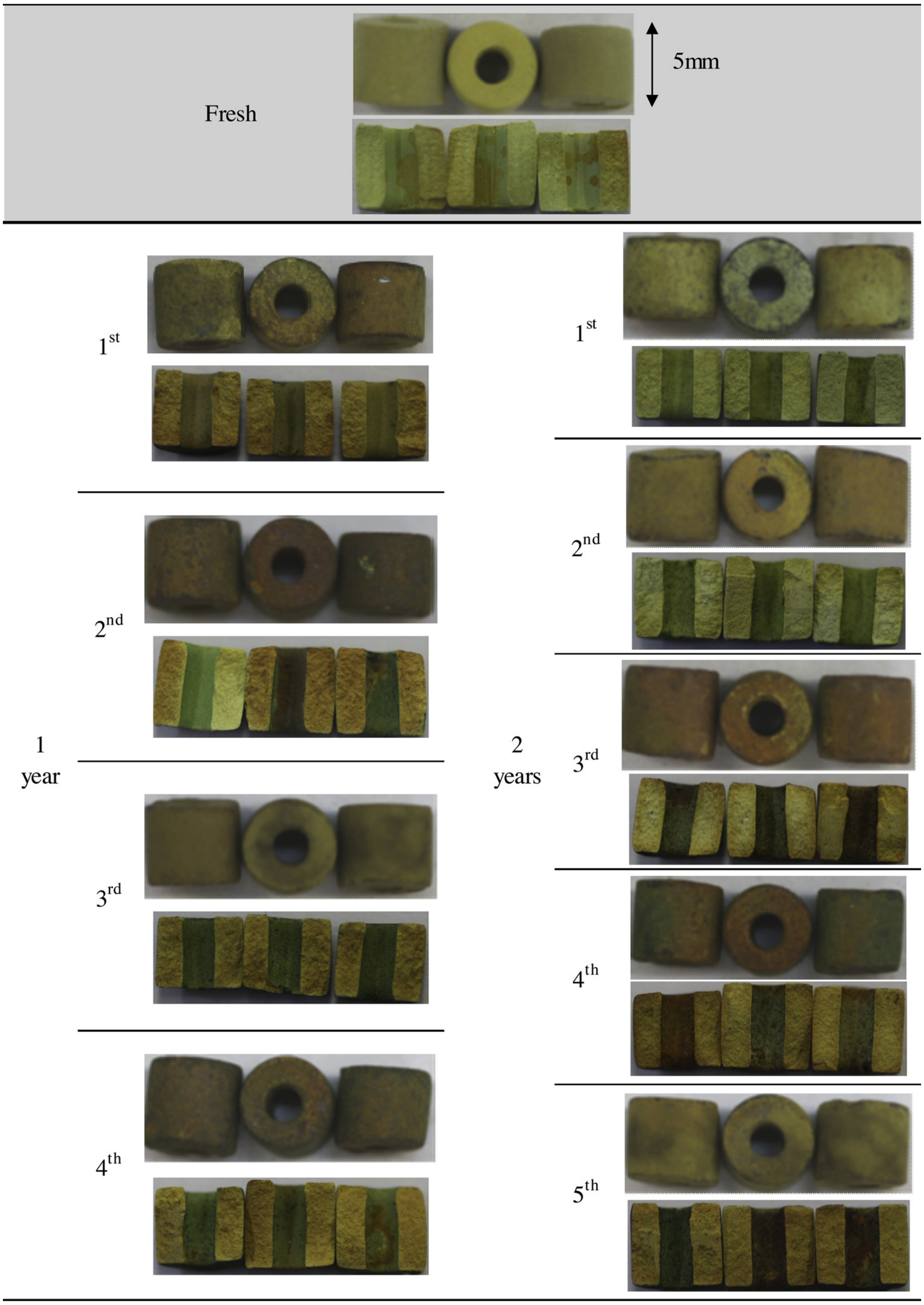
The activities of the fresh and used catalysts were evaluated using a fixed-bed reactor (inner diameter = 29 mm). The catalyst was mixed with an equal volume of diluent (14 mL, graphite pellets) and transferred to a Pyrex reaction tube. The remaining space in the reaction tube was filled with glass beads. The reaction conditions were controlled at a reactant ratio of $HCl:C_2H_4:O_2:N_2 = 2.0:1.0:0.4:2.8$ and a gas hourly space velocity (GHSV) of 400 $h^{-1}$. The reaction temperature was controlled so that the inlet temperature of the catalyst layer was 493 K.

The catalytic activity was derived by dividing the amount of ethylene conversion by the mass of the catalyst and reaction time for the temperature conditions described above. The activity of the fresh catalyst was considered the standard, and the activity of the used catalysts was presented as the relative activity, based on an initial catalyst performance of 100%.

### 2.4. Characterization of the catalyst

The shape retention rate of the used catalyst was determined by the weight ratio of particles remaining on the top of a 2.8-mm mesh sieve. The surface area and pore volume were measured using the $N_2$ adsorption method (Microtrac bell BELSORP mini). Prior to the measurement, samples (0.1–0.2 g) were weighed following vacuum drying at 473 K for 4 h. The fracture strength in the lateral direction of the cylindrical catalyst used was measured using a digital push–pull gauge (Aikoh Engineering MODEL-RX).

The amounts of Cu and K supported in the catalyst were measured



**Scheme 2.** Oxychlorination with a Cu(II) chloride catalyst.

using X-ray fluorescence (XRF, Rigaku ZSX Primus II). Five standard samples were prepared with different amounts of Cu and K using the pore-filling method; a calibration curve was prepared based on the measurement results of these standard samples. In pretreatment, the sample was crushed into powder and dried. Approximately 3 g of the powdered sample was added into a 30-mm-φ plate ring followed by pressing at 11 MPa for 40 s and 5.0 MPa for 20 s. Before measurement, the sample plate was vacuum-dried to remove moisture.

Elemental mapping of the cross-section of the catalyst was performed using electron probe microanalysis (EPMA; Shimadzu EPMA-1610; accelerating voltage: 15 kV, illumination current: 30 nA, beam diameter: 20 μm, analysis area: 10.752 × 10.752 mm). Prior to the measurement, the upper surface of the cylindrical catalyst was polished and coated with carbon.

### 2.5. Hydrothermal test

Hydrothermal tests were carried out on the γ-alumina substrate and on the fresh catalyst using a stainless steel pressure vessel. The γ-Alumina or fresh catalyst (5 g) and 1 mol/L hydrochloric acid (5 mL) were loaded into a Teflon container (internal volume = 37 mL), separated by a Teflon mesh. The Teflon container was placed into a stainless steel container and treated at 473 K for a predetermined time. Thereafter, the samples were dried at 473 K for 1 h. The surface area and the pore volume of the samples were measured.

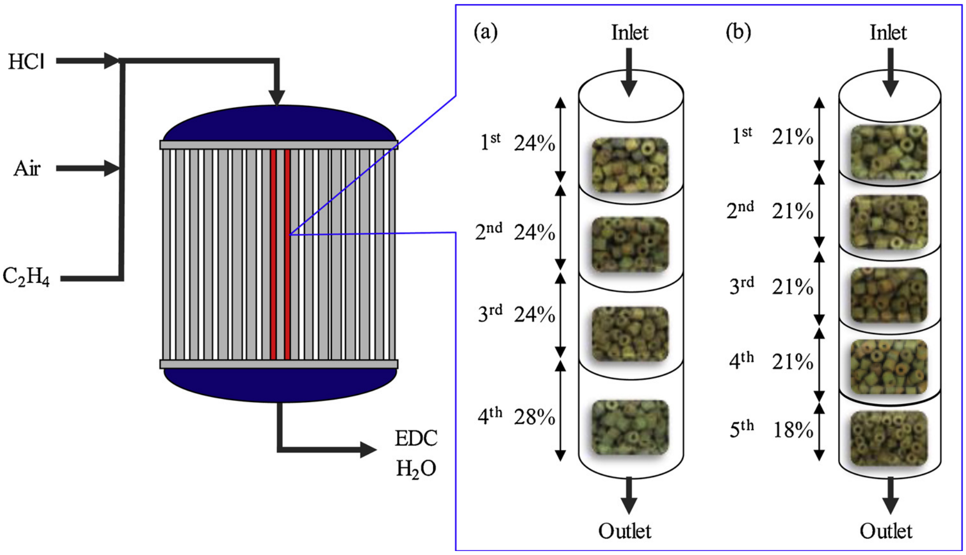


**Fig. 1.** Divided samples from the commercial plant after (a) 1 year and (b) 2 years.

## 3. Results and discussion

### 3.1. Appearance and shape of catalysts used in the commercial plant

Fig. 2 shows the appearance of the fresh and used catalysts. The upper side of each column is the appearance of a cylindrical outer surface, and the lower side is of a cylindrical cross section. In the fresh catalyst, the appearance of the cylindrical outer surface and cross-section were likewise pale yellow-green. Vetrivel et al. reported a spent catalyst with a dark core as compared to a spherical surface [27,28]. Furthermore, they reported that $CuAlO_2$ was formed in the core of the spherical spent catalyst. In contrast, all of our cylindrical shape used catalysts were darker in color than the respective fresh ones. This color change was more significant on the cylindrical outer surface. In addition, there was a difference between the appearance of the cylindrical outer surface and the cross section in the used catalysts. We suggest that the changes in the catalyst occurred mainly on the cylindrical outer surface rather than in the bulk. Fig. 3 shows the shape retention, which indicates mechanical durability of the catalyst after 2 years of operation. It has been reported that the large pressure loss caused by powdering of the catalysts often hinders long-term plant operation [15]. Therefore, changes in strength and shape retention are important factors for commercial plant operation. The shape retention rate of the used catalyst was determined by the weight ratio of particles remaining on the top of a 2.8-mm mesh sieve. In the 1st and 2nd positions, the retention rate fell below 90%, with the 2nd position falling the lowest. This suggests that the load on the front side of the reaction tube was high for the 2 years of operation. On the other hand, in the 3rd to 5th positions, the shape retention rate was 90% or more, and the overall average retention rate was ~90%. The tested catalysts showed high durability for 2 years of operation in the commercial plant [29].

Fig. 4 shows the fracture strength of the used catalysts. The fracture strength of the fresh catalyst was 27 N, which decreased to 13–20 N after 1 year and to 13–18 N after 2 years, indicating that there was no significant change in fracture strength. The fracture strength was lowest at the 2nd position for both years. At the 2nd to 5th positions, after 2 years a correlation was found between the fracture strength and shape retention rate. It is estimated that the decrease in shape retention ratio at the 2nd to 5th positions was dominated by physical cracking and powdering due to the decrease in fracture strength. On the other hand, the strength at the 1st position was higher, but the shape retention was similar to those at the other positions. As described in Section 3.4, weight loss due to sublimation of CuCl is presumed to have a major influence at the 1st position. Therefore, we speculate that the ratio of shape retention was 90% or less despite maintaining the high fracture strength of the 1st position catalyst. In our test catalysts, it was shown that cracks and dust due to the decrease in fracture strength were not dominant deterioration factors in plant operation.

### 3.2. Physicochemical properties of catalysts

Table 1 shows the Brunauer–Emmett–Teller (BET) specific surface area and pore volume of the catalysts. Both properties were lower in the used catalysts than the fresh ones at all positions. This indicates that the decrease in pore volume and in BET specific surface area occurred at the same time. The decrease in BET specific surface area was more pronounced; the used catalysts were reduced to $68\sim85\ m^2/g$ and the fresh catalyst to $112\ m^2/g$. In particular, the BET specific surface area in the 2nd position decreased to nearly 60% of the initial value. This decreasing trend was similar to the decrease in fracture strength and shape retention. Furthermore, such a decrease in BET specific surface area was observed in spent catalysts by Vetrivel et al. [28]. To clarify the cause, we conducted hydrothermal tests on the γ-alumina substrate and the fresh catalyst. Fig. 5 shows the change in BET specific surface area and pore volume after the hydrothermal tests. Both properties decreased with increasing hydrothermal treatment time, although the decrease was smaller in the catalyst than in the alumina substrate. This is probably because of the reduced contact between water and the alumina surface by the supported metal. Fig. 6 shows the pore distribution and pore volume of the fresh catalyst and the catalyst used for 2 years, alumina substrate, and hydrothermally treated sample. In the catalysts used for two years in commercial plants, a decrease in pore size of 3–10 nm and an increase in pore size of 10–50 nm were observed in comparison with fresh ones. The changes in the catalysts used in commercial plants were reproduced in the sample wherein the alumina substrate was hydrothermally treated for 5 h. From these results, we speculated that grain growth of γ-alumina due to hydrolysis was the cause of the decrease in BET specific surface area and pore volume. Therefore, we infer that in the used catalysts, the decrease in BET specific surface area and pore volume occurs for the whole of the downstream side, where the concentration of the by-produced water increases.

### 3.3. Performance of catalysts used in the commercial plant

Table 2 shows the activity of the oxychlorination catalysts. The

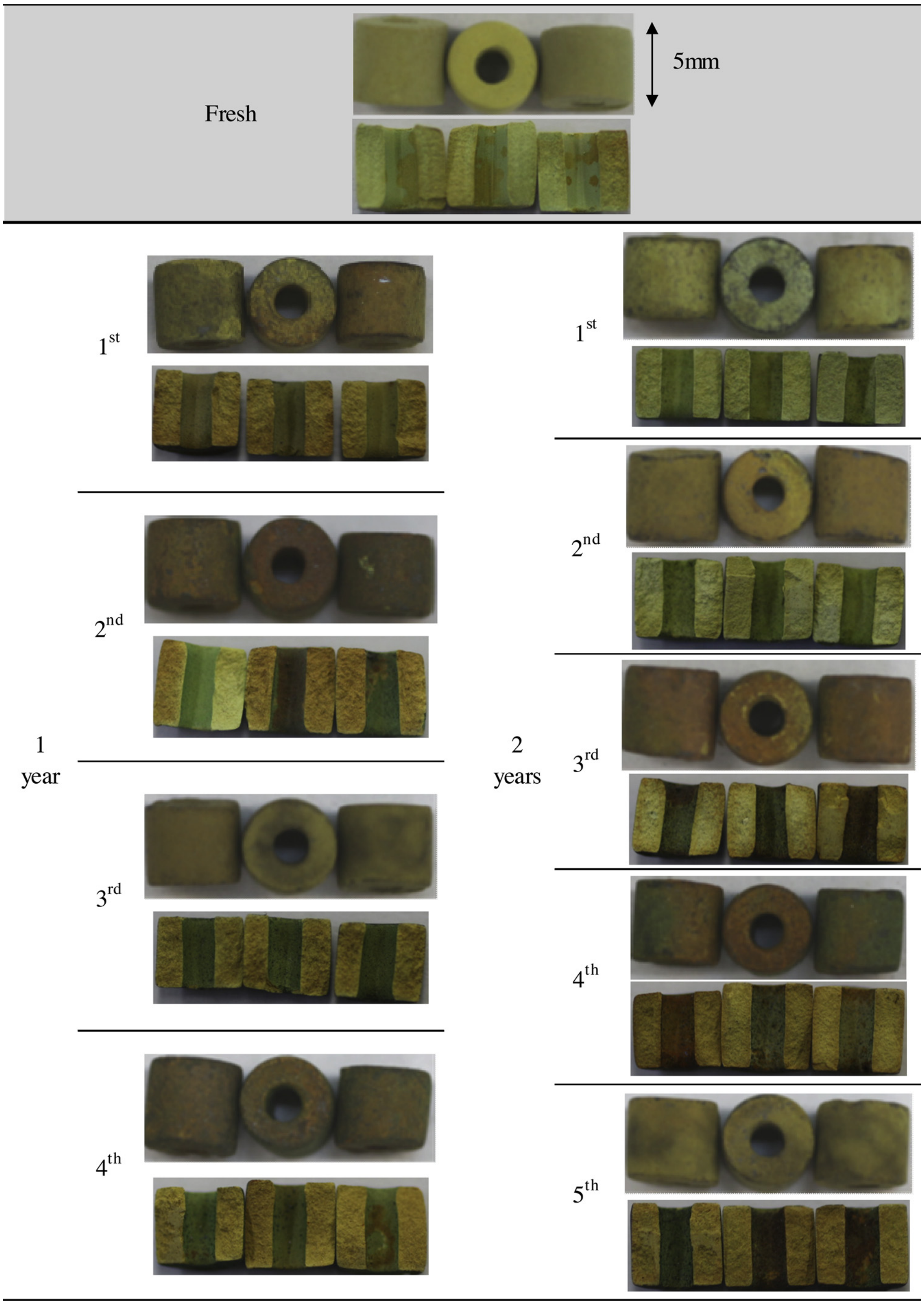


**Fig. 2.** Appearance of fresh and used catalysts in the commercial plant.

activity given here is the relative activity, based on an initial catalyst performance of 100%. In the used catalysts, the activity decreased with increasing operation time. The catalysts sampled from the inlet side (1st and 2nd positions) were clearly deactivated, but those from the middle and outlet side (3rd, 4th, and 5th positions) were not notably reduced. In particular, the specific activities decreased to 56% and 69% for the 1st and 2nd positions, respectively, in the catalyst used for 2 years. This suggests that the load on the front side of the reaction tube was high for the 2 years of operation.

Fig. 7 shows the average temperature of the reaction tube during the commercial plant test. The operating temperatures of commercial plants are confidential and not reported. A sharp peak appeared at the 2nd and 3rd positions, which shows that the reaction progressed mainly on the front side of the temperature peak position. Therefore, we infer that the activity decline of the 1st and 2nd positions were significant.

Table 3 shows the selectivity of the oxychlorination catalysts. The main product of the reaction of any catalyst was EDC. In addition to EDC, trace amounts of chlorinated by-products, as well as carbon monoxide and carbon dioxide, were produced, as found in other literature [30]. The EDC selectivity of the used catalysts decreased slightly as compared to that of the fresh catalyst. With the used catalysts, no significant change was observed in the formation rates of carbon monoxide and carbon dioxide, but there was an increase in the ethyl chloride (EC) and VCM selectivity.

### 3.4. Chemical composition of catalysts

Table 4 shows the chemical compositions of the catalysts. The

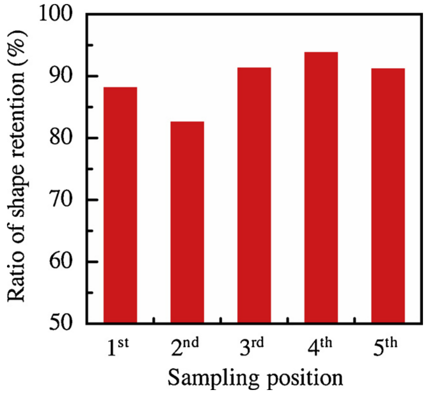


**Fig. 3.** Shape retention of the used catalyst after 2 years of operation.

**Table 1**
Physical Physical properties of the oxychlorination catalysts talysts.

| Catalyst | | BET[a)] surface ($m^2$/g) | Pore volume (ml/g) |
|---|---|---|---|
| Fresh | | 112 | 0.30 |
| 1 year | 1st | 80 | 0.30 |
| | 2nd | 68 | 0.25 |
| | 3rd | 78 | 0.27 |
| | 4th | 83 | 0.29 |
| 2 year | 1st | 85 | 0.31 |
| | 2nd | 71 | 0.27 |
| | 3rd | 73 | 0.27 |
| | 4th | 76 | 0.29 |
| | 5th | 76 | 0.28 |

[a)] Brunauer–Emmett–Teller.

amount of K in the used catalysts was almost the same as that in the fresh catalyst, while the amount of Cu decreased with operation year. It has been found that CuCl formed in the oxychlorination catalytic cycle was sublimable. It appears that this sublimation of CuCl reduced the amount of Cu in the used catalysts [31–33]. This was most prominent on the inlet side (1st and 2nd positions) where the reaction primarily occurs. At the 1st and 2nd positions, the alumina surface could be exposed owing to the decrement of Cu. Finocchio et al. [30] performed pulse reaction experiments on catalysts with 1%–9% supported Cu. They found that catalysts with a small amount of supported Cu had low EDC selectivity and increased formation rate of ethyl chloride and VCM. These results were consistent with the performance of used catalysts in the 1st and 2nd positions. In addition, Muddada et al. [22], Shalygin et al. [34], and Carmello et al. [35] showed that alumina serves as the active site of VCM production by dehydrochlorination of EDC in experiments feeding EDC to alumina. Muddada et al. [36] also examined the relationship between the concentration of Lewis acid sites on the catalyst and the by-products of the oxychlorination reaction. It was confirmed that the by-productivity of ethyl chloride and VCM was increased in catalysts with high Lewis acid concentrations. From these reports and results, it is assumed that the exposed alumina surface acted as a Lewis acid, which caused the increase in ethyl chloride and VCM in the used catalysts at the 1st and 2nd positions.

In the used catalysts, iron was detected in addition to the components of the fresh catalyst. In our commercial plant test, the origin of the iron was unknown. However, Aharoni and Inbar [37], Kurta et al. [38], and Flid [18] stated that in a fluidized bed oxychlorination reactor, iron penetration is usually due to the erosion of industrial reactor walls. Todo et al. [3] evaluated the oxychlorination performance of various metal chloride catalysts, and stated that the main product of oxychlorination with $FeCl_3$-supported catalyst was ethyl chloride. Furthermore, iron oxide is known to react with hydrogen chloride to form iron chloride [39]. The iron component observed in the used catalyst is likely to have produced iron chloride because of the prolonged exposure to hydrogen chloride gas at high temperatures in the plant. From this finding, we speculate that iron chloride, acting as a Lewis acid, caused an increase in the amount of ethyl chloride and VCM in used catalysts at the 3rd to 5th positions.

Fig. 8 shows the results of EPMA of Cu and K in the cross-section of the cylindrical catalyst. Cu and K were uniformly distributed in the fresh catalyst, whereas in the 1-year-used catalyst at the 3rd position and 2-years-used catalyst at the 3rd to 4th positions, Cu content increased on the cylindrical surface layer with respect to the bulk. This trend was particularly notable in the 1-year-used catalyst at the 3rd position. In contrast, in the 1-year-used catalyst at the 1st to 2nd positions and in the 2-years-used catalyst at the 1st to 2nd positions, Cu content was decreased throughout the catalyst, especially in on cylindrical surface layer. In general, since the reaction mainly proceeds on the surface of the solid catalyst, it was presumed that the Cu in the cylindrical surface layer was remarkably sublimated. Vetrivel et al. [28] studied the X-ray line profile of fresh and deactivated catalysts, and reported that Cu was abundant on the fresh catalyst surface but reduced on the deactivated catalyst surface. These findings were consistent with our EPMA results for the used catalyst at the 1st and 2nd position. Furthermore, the decrease in the Cu content by CuCl sublimation might be related to the heat of reaction and the rate of formation of CuCl by the reduction of $CuCl_2$. From these results, we infer that in the 1st and 2nd positions, where the reaction primarily progressed, Cu was reduced from the cylindrical surface layer by sublimation of CuCl, while at the 3rd and 4th positions, further downstream, sublimed CuCl was deposited on the cylindrical surface layer. $CuCl_2$ reduction would not have predominantly occurred at the 3rd position despite the high average temperature. In contrast, no difference in the distribution of K was observed

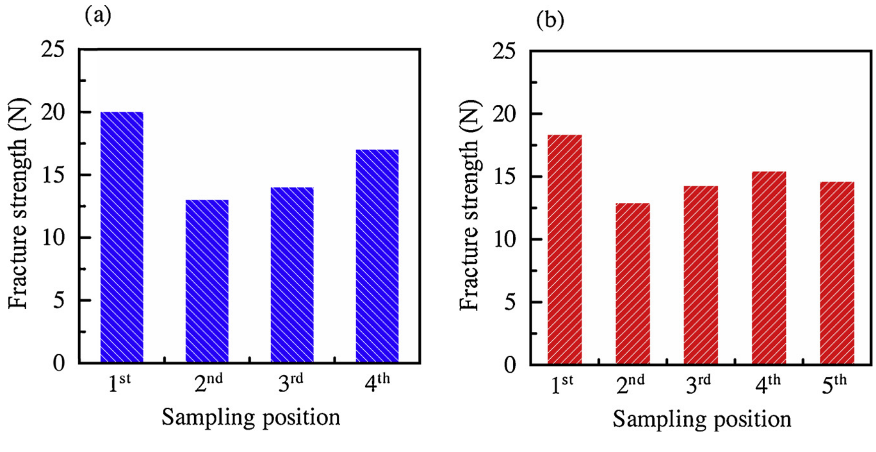


**Fig. 4.** Fracture strength of the used catalysts after (a) 1 year and (b) 2 years.

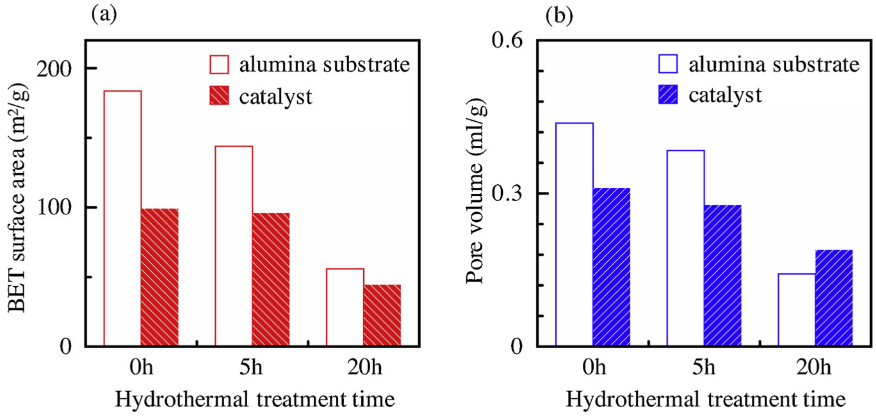


**Fig. 5.** Results of hydrothermal tests. (a) Brunauer–Emmett–Teller (BET) specific surface area, (b) pore volume.

between the fresh catalyst and the used catalysts.

### 3.5. *Influence of changing chemical composition on catalytic performance*

Fig. 9 shows the oxychlorination activity of the catalysts sampled from each position of the reactor, in comparison with the BET specific surface area and Cu content. The activity reported here is the relative activity, based on an initial catalyst performance of 100%. As shown in Fig. 9, the used catalysts for both the 1st and the 2nd years had similar trends, except that inactivation on the inlet side was greater after 2 years than after 1 year. In both the 1st and 2nd year, specific activity peaked slightly upstream from the last position. In other words, the decrease in BET specific surface area (and hence, pore volume) did not correlate with the activity, showing it was not the main deactivation factor in catalysts used for 2 years. The BET specific surface area on the inlet side (1st position) was high in contrast to the activity, and decreased to ~70% in the 3rd–5th positions, whereas the specific activity was maintained at 85% or more. In contrast, the tendency of activity corresponds considerably with the order of Cu content. These findings indicate that the sublimation of CuCl, caused by the high exothermic energy profile at the inlet side was one of the factors of deactivation for the $CuCl_2$-$KCl/Al_2O_3$ catalyst. In addition, peak activity appeared at the 3rd position during the 1st year, and at the 4th position in the 2nd year owing to deposition of sublimated CuCl from the upper stream. Changes in the catalyst components due to CuCl sublimation and deposition were presumed to be closely related to the catalyst activity.

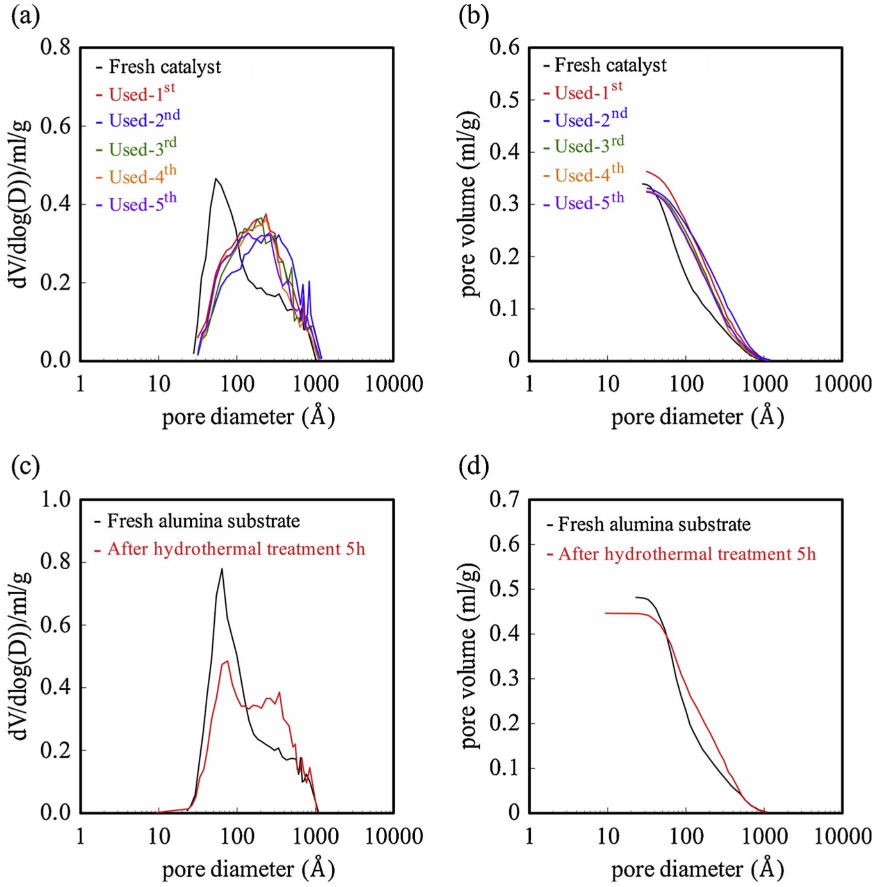


**Fig. 6.** Pore distribution and pore volume. (a) Pore distribution of fresh catalyst and catalyst used for 2 years, (b) Pore volume of fresh catalyst and catalyst used for 2 years, (c) Pore distribution of alumina substrate and hydrothermal test sample, (d) Pore volume of alumina substrate and hydrothermal test sample.

**Table 2**

Activities of the oxychlorination catalysts.

| Catalyst | Amount of (mmol) | | Amount of ethylene (mmol/g· h) | Activity (%) |
|---|---|---|---|---|
| Fresh | 44 | | 3.8 | 100 |
| 1 | 1st | 29 | 2.7 | 70 |
| | 2nd | 45 | 3.1 | 82 |
| | 3rd | 64 | 4.3 | 112 |
| | 4th | 46 | 3.5 | 93 |
| 2 | 1st | 38 | 2.1 | 56 |
| | 2nd | 47 | 2.6 | 69 |
| | 3rd | 61 | 3.6 | 96 |
| | 4th | 45 | 3.6 | 94 |
| | 5th | 41 | 3.2 | 85 |

Reaction condition: a reactant ratio of HCl:$C_2H_4$:$O_2$:$N_2$ = 2.0:1.0:0.4:2.8, a gas hourly space velocity (GHSV) of 400 $h^{-1}$, 493 K -2 cm from inlet of catalyst layer in atmospheric pressure.

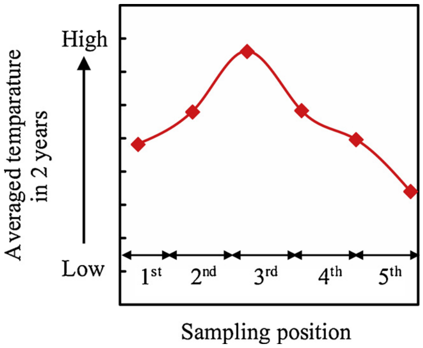


**Fig. 7.** Average temperature of the reaction tube during the commercial plant test.

**Table 3**

Selectivities of the oxychlorination catalysts.

| Catalyst | | Selectivity(%) | | | | | |
|---|---|---|---|---|---|---|---|
| | | EDC[a)] | VCM[b)] | EC[c)] | TCE[d)] | CO | $CO_2$ |
| Fresh | | 99.5 | 0.0 | 0.1 | 0.1 | 0.1 | 0.2 |
| one | 1st | 99.5 | 0.0 | 0.1 | 0.1 | 0.1 | 0.2 |
| | 2nd | 99.6 | 0.0 | 0.1 | 0.1 | 0.1 | 0.1 |
| | 3rd | 99.4 | 0.0 | 0.1 | 0.1 | 0.2 | 0.2 |
| | 4th | 99.5 | 0.0 | 0.2 | 0.1 | 0.1 | 0.1 |
| two | 1st | 99.4 | 0.0 | 0.2 | 0.1 | 0.1 | 0.2 |
| | 2nd | 99.4 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 |
| | 3rd | 99.3 | 0.1 | 0.2 | 0.1 | 0.1 | 0.2 |
| | 4th | 99.4 | 0.1 | 0.2 | 0.1 | 0.1 | 0.1 |
| | 5th | 99.3 | 0.1 | 0.3 | 0.1 | 0.1 | 0.1 |

Reaction condition: a reactant ratio of HCl:$C_2H_4$:$O_2$:$N_2$ = 2.0:1.0:0.4:2.8, a gas hourly space velocity (GHSV) of 400 $h^{-1}$, 493 K -2 cm from inlet of catalyst layer in atmospheric pressure.

[a)] EDC; ethylene dichloride.

[b)] VCM; vinyl chloride monomer.

[c)] EC; ethyl chloride, d) TCE; trichloroethane.

**Table 4**

Chemical compositions of the catalysts.

| Catalyst | | Amount | | | | |
|---|---|---|---|---|---|---|
| | | Cu (wt%) | K (wt%) | Fe (wt%) | others (wt%) | K/Cu (mol/mol) |
| Fresh | | 6.2 | 2.6 | N.D. | 91.3 | 0.68 |
| 1 year | 1st | 5.0 | 2.5 | N.D. | 92.5 | 0.81 |
| | 2nd | 5.0 | 2.5 | N.D. | 92.5 | 0.81 |
| | 3rd | 6.0 | 2.5 | 0.1 | 91.4 | 0.68 |
| | 4th | 5.7 | 2.5 | 0.7 | 91.1 | 0.71 |
| 2 years | 1st | 4.6 | 2.4 | N.D. | 93.0 | 0.85 |
| | 2nd | 4.8 | 2.4 | 0.1 | 92.7 | 0.81 |
| | 3rd | 6.1 | 2.4 | 0.3 | 91.2 | 0.64 |
| | 4th | 6.2 | 2.4 | 0.3 | 91.1 | 0.63 |
| | 5th | 5.8 | 2.5 | 0.4 | 91.3 | 0.70 |

Fig. 10 shows the relationship between the K-to-Cu ratio (K/Cu) and the activity of the fresh and used catalysts. The K-to-Cu ratio was determined from the amount of each element measured by X-ray fluorescence. The fresh catalysts shown here were prepared to have different K/Cu ratios, with approximately the same amount of Cu (5.9–6.2 wt%), separately from the catalyst loaded in a commercial plant. A strong linear correlation was found between the specific activity and the K/Cu ratio in the fresh catalysts. Rouco [21] compared the oxychlorination catalytic activities of $CuCl_2/\gamma\text{-}Al_2O_3$ and $CuCl_2\text{-}KCl/\gamma\text{-}Al_2O_3$ and reported that the catalyst with added KCl had lower activity than the $CuCl_2/\gamma\text{-}Al_2O_3$ catalyst. Arcoya et al. [16] and Dmitrieva et al. [40] examined the effect of the addition of alkali chlorides on the $CuCl_2/\alpha\text{-}Al_2O_3$ catalyst. They found that activity decreased linearly with increasing KCl content in the catalysts with high KCl loadings. They considered that the decrease in activity was due to KCl being inactive and interfering with the contact between the reactants and $CuCl_2$. In addition, Prasad and Rao [41] measured the chemisorption rate of ethylene to $CuCl_2/\gamma\text{-}Al_2O_3$ or $CuCl_2\text{-}KCl/\gamma\text{-}Al_2O_3$ at −78 °C. They showed that the amount of ethylene chemisorption decreased linearly as the K/Cu ratio decreased from 0.5 to 0.14 (Cu/K atomic ratio from 2 to 7 [41]), and concluded that the amount of ethylene chemisorption at low-temperature may be related to the active sites on the oxychlorination catalysts.

These reports show good agreement with our results. In the used catalysts, the K/Cu ratio increased due to the decrease in Cu caused by sublimation. Furthermore, the activity decreased concurrently with the increasing K/Cu ratio. These results suggests that the main cause of used catalyst deactivation was the increase in the K/Cu ratio due to Cu sublimation. In the catalysts used for 1 year, the activity was equivalent to the fresh ones with low K/Cu ratios, but was lower than the fresh catalysts with high K/Cu ratios. However, in the 1-year-used catalyst at the 3rd position, the activity was higher than the fresh catalyst. Elemental mapping for the 1-year-used catalyst at the 3rd position (Fig. 8) show that Cu content increased on the cylindrical surface layer with respect to the bulk, implying that the K/Cu ratio was lower on the surface of the 1-year-used catalyst at the 3rd position than on the surface of the fresh catalyst. Therefore, in the 1-year-used catalyst at the 3rd position, the activity was higher than that of the fresh catalyst. In the catalysts used for 2 years, the activity of all layers declined further; in particular, the activities of catalysts with high K/Cu ratios were greatly reduced compared with the catalysts used for 1 year. Elemental mapping in the 2-years used catalyst at the 2nd position (Fig. 8) showed that Cu was distributed more toward the surface than the center of the ring in the fresh catalyst, but was reduced at the surface in the used catalyst. This means that the K/Cu ratio was higher on the surface of the used catalyst than on that of the fresh catalyst, especially at the 1st and 2nd positions. Therefore, the activity of the 2-years used catalyst was inferred to be lower than that of fresh catalyst. These findings suggest that changes resulting from the use of catalysts in commercial plants occur primarily on the surface of the catalyst. Therefore, it is important to obtain the composition of the surface, which contains the active sites, to investigate the performance of catalysts for use in commercial plants. From these results, we concluded that the main cause of catalyst deactivation during operation was the increase in the K/Cu ratio due to Cu sublimation. A strong correlation between K/Cu and activity was confirmed, suggesting that the change in the K/Cu ratio may have had a dominant influence on the active site. Lamberti et al. reported that the

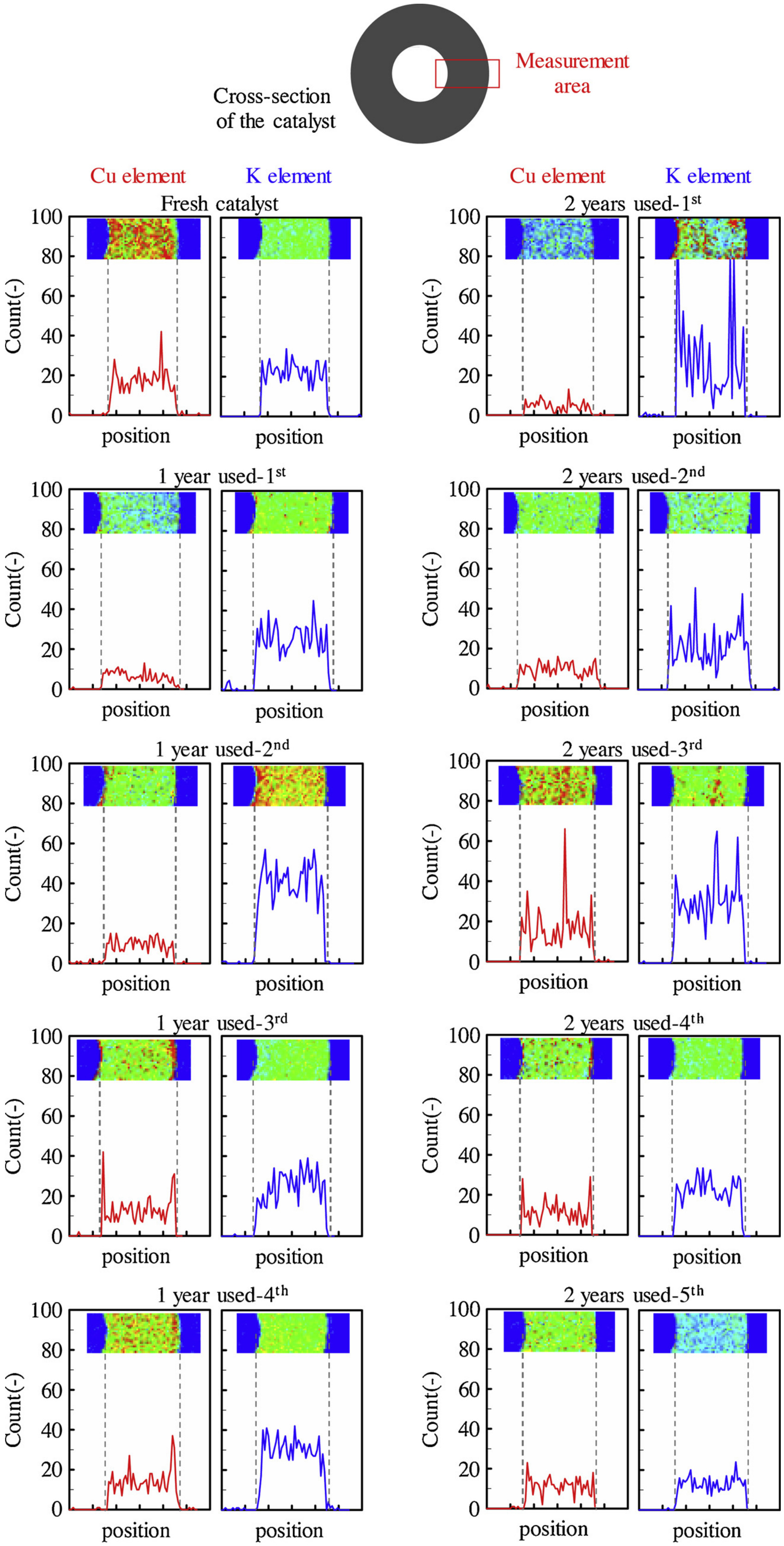


**Fig. 8.** Cu and K distribution in the fresh and used catalysts. Data from electron probe microanalysis (EPMA). Samples were cut along the length of the cylinder.

active phase of $CuCl_2$-$KCl/Al_2O_3$ is a mixed chloride ($K_xCuCl_{2+x}$) phase that reduces the ability of the active surface to adsorb ethylene and/or transfer two Cl atoms to each ethylene molecule [17,20]. Therefore, it is presumed that the amount of the ($K_xCuCl_{2+x}$) phase increased by an increase in the K/Cu ratio in our used catalysts as well. In the future, we will carry out a detailed evaluation of the change of catalyst by

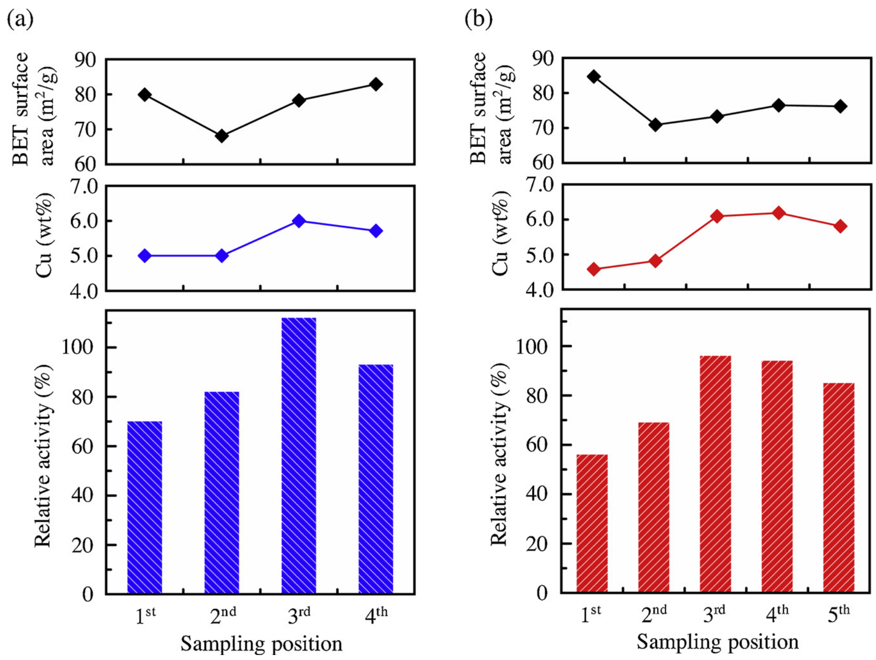


**Fig. 9.** Oxychlorination performance change of used catalysts after (a) 1year and (b) 2 years. The reaction conditions were controlled at a reactant ratio of $HCl:C_2H_4:O_2:N_2$ = 2.0:1.0:0.4:2.8, a gas hourly space velocity (GHSV) of 400 h-1, the reaction temperature of 493 K.

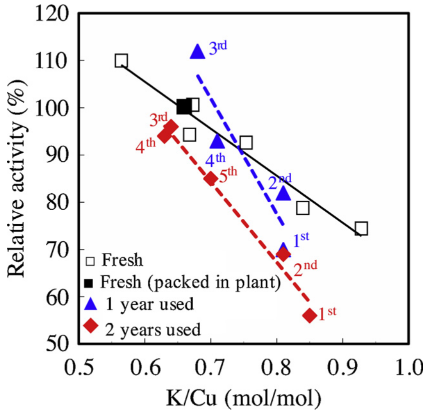


**Fig. 10.** Activity vs. K/Cu ratio. The reaction conditions were controlled at a reactant ratio of $HCl:C_2H_4:O_2:N_2$ = 2.0:1.0:0.4:2.8, a gas hourly space velocity (GHSV) of 400 h-1, the reaction temperature of 493 K.

implementing a kinetic study and electronic state analysis of Cu in the used catalysts.

## 4. Summary and conclusions

An oxychlorination catalyst was investigated after operation for 2 years in a commercial plant, to determine the cause of deterioration during long-term operation. The oxychlorination performance of the $CuCl_2$-$KCl/Al_2O_3$ catalyst gradually declined, which would seriously affect the stable operation of a commercial plant. In samples of used catalysts, cracking and powdering were confirmed as the main reasons for declining catalyst activity due to operation of the plant. However, our test catalyst had sufficient mechanical durability after 2 years of operation. Furthermore, by investigating the relationships between catalyst performance and changes in physicochemical characteristics, a clear correlation was found between the sublimation of Cu and activity, whereas a decrease in BET specific surface area and pore volume did not contribute to the decrease in activity. We speculate that the increase in the K/Cu ratio due to sublimation of Cu caused a change in the state of the active site. We conclude that this state change is the dominant factor in the depreciation of plant operation life. Therefore, it is important to control the K/Cu ratio and adjust the dilution rate of the catalyst at each position in the plant for preventing loss of catalytic activity due to the sublimation of Cu.

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