

## [Regular Paper]

Effective Dechlorination of 2-Chloropropene to Propylene on a Metallic Nickel Catalyst Supported on  $\gamma$ -AluminaShigeru SUGIYAMA\*<sup>†1)</sup>, Yuka HIWADA<sup>†2)</sup>, Ryota YAHARA<sup>†3)</sup>,  
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We previously reported that the reductive conversion of 2-chloropropene (2-PEN) on  $\gamma$ -alumina-supported palladium catalysts showed high activity at 348 K. However, 2-chloropropane (2-PAN), propylene, and propane were produced non-selectively in this catalyst system, so industrial development would require separation process. In the present study, an alumina-supported nickel catalyst achieved a highly selective conversion of 2-PEN to propylene. For example, the propylene selectivity reached 95.7 % and conversion of 2-PEN was 15.0 % on the catalyst loaded with 10 % nickel at 473 K. However, the propylene yield was only 14.3 %, so the reaction was examined at 623 K, which resulted in 75.6 % conversion of 2-PEN and 78.6 % selectivity to propylene, with an adequate 59.4 % yield. Importantly, no propane was produced under these conditions, eliminating the need to separate propane and propylene. We concluded that by using nickel as a catalyst, an excessive reduction of propylene to propane could be suppressed.

**Keywords**

2-Chloropropene, Propylene, Dechlorination, Hydrogenation, Nickel catalyst

**1. Introduction**

Organic chlorides are widely produced in Japan, for consumption by the thriving petrochemical and soda industries. For example, allyl chloride has various applications such as a raw material and intermediate for the manufacture of industrial products, pharmaceuticals, and agricultural chemicals, and is produced by many companies in Japan<sup>1)~5)</sup>. One of the typical methods for the production of allyl chloride utilizes the reaction between propylene and chlorine, but various by-products are also formed<sup>1)~5)</sup>. Our previous study intended to effectively utilize such by-products focused on 2-chloropropene, which is a major by-product<sup>6),7)</sup>. Reduction of 2-chloropropene (2-PEN) with a commercially available alumina-supported palladium catalyst proceeded well at a low temperature of 348 K for the nonselective conversion of 2-PEN into 2-chloropropane (2-PAN), propylene, and propane. However, propane

obtained from 2-PEN can only be used as a fuel. Furthermore, 2-PAN and propylene, which are common as chemical product precursors<sup>7)</sup>, could not be obtained selectively with that catalyst system. In particular, co-produced propylene and propane are extremely difficult to separate. Therefore, utilization of these by-products will remain a difficult unless nonselective co-production is resolved. Modern academic research rarely considers the catalytic conversion of organic chlorides. In contrast, industrial interests widely adopt the catalytic conversion of organic chlorides, and patents are actively issued. Therefore, our group planned further research.

Nonselective conversion was thought to originate from the too high activity of the palladium catalyst, resulting in the deep reduction of propylene to propane. Therefore, reductive conversion of 2-PEN to propylene on a  $\gamma$ -alumina-supported nickel catalyst, which typically has low activity but is a promising reductive substance, was examined to suppress the deep reduction of propylene to propane. Reduction of propylene to propane using palladium and nickel catalysts has long been investigated<sup>8)~10)</sup>. Our research identified the possibil-

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ity of suppressing the reduction of propylene to propane from the preliminary experiments on nickel catalyst supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Based on this background, this study investigated the reduction behavior of 2-PEN with the alumina-supported nickel catalyst.

## 2. Experimental

### 2.1. Catalyst Preparation

In the present study, the catalysts are referred to as Ni(*x*)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (*x* = 5, 10, 15, and 20), in which “*x*” indicates the Ni content by weight %, defined as  $100 \times \text{Ni [g]} / (\text{Ni [g]} + \gamma\text{-Al}_2\text{O}_3 \text{ [g]})$ . For example, Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was prepared by the impregnation method. An aqueous solution (30 mL) containing 2.310 g of dissolved Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (FUJIFILM Wako Pure Chemical Corp.) was stirred with 4.196 g of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-9 reference catalyst, Catalysis Society of Japan). The obtained suspension was evaporated at 353 K and dried at 393 K for 12 h. Then, the resultant solid was calcined at 773 K for 2 h. Before evaluation of the catalytic activity, the solid was pelletized to 1.18–1.70 mm and loaded into a reactor. Then, the solid was reduced at 923 K for 1.0 h in the reactor using hydrogen (45 mL/min) diluted with nitrogen (15 mL/min), which was followed by adjusting the reaction temperature under nitrogen flow.

### 2.2. Characterization

The nitrogen adsorption isotherms of the catalysts pretreated at 473 K for 5 h were measured using a BELSORPmax12 (MicrotracBEL Corp.) at 77 K to estimate the specific surface area of Ni(5)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, Ni(15)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and Ni(20)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 198, 138, 172, and 155 m<sup>2</sup>/g, respectively. A smartLab/R/INP/DX (Rigaku Corp.) with a Cu K $\alpha$  radiation monochromator at 45 kV and 150 mA was used for X-ray diffraction (XRD) analysis. An EXSTAR6000 (Seiko Instruments Inc.) under air flow (100 mL/min) at a heating rate of 8 K/min from 298 to 1073 K was employed for thermogravimetric (TG) analysis. A PHI-5000Versa-Probe II (ULVAC-PHI Inc.) was used for the X-ray photoelectron spectroscopy (XPS) analysis of the catalyst surface using Al K $\alpha$  radiation that were calibrated based on a C 1 s peak at 284.6 eV. Argon ion sputtering was carried out at 2 kV for 2 min.

### 2.3. Evaluation of Catalytic Performance

The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor at atmospheric pres-

sure. The reactor consisted of a quartz tube with an I.D. of 9 mm and a length of 35 mm that was sealed at each end to a 4 mm I.D. quartz tube for a total length of 25 cm. The catalyst (*W* = 1.0 g or 1.4 g) was held in place in the enlarged portion of the reactor by two quartz wool plugs. The reactant (2-PEN) was introduced to the main flow of mixed hydrogen and nitrogen gases by saturating a separate stream of nitrogen with 2-PEN at 263 K. The partial pressure of 2-PEN was estimated using the Antoine equation<sup>11</sup>). In all experiments, the temperature of the catalyst was raised to 923 K while maintaining a continuous flow of nitrogen. Then, pretreatment was performed for 1.0 h using a gaseous mixture of hydrogen (45 mL/min) and nitrogen (15 mL/min). After pretreatment, the H<sub>2</sub> flow was stopped and the temperature was adjusted to a reaction level. Then, a reactant gaseous mixture consisting of 2-PEN, H<sub>2</sub>, and N<sub>2</sub> was introduced into the reactor at each partial pressure of  $P(2\text{-PEN}) = 8.8$  kPa,  $P(\text{H}_2) = 13.5$  kPa or 20.3 kPa, and  $P(\text{N}_2) = 79.0$  kPa or 72.2 kPa with a total flow rate of  $F = 90$  mL/min. Under these conditions, homogeneous reactions were not detected. The reaction was monitored using two gas chromatographs (GC-8A and GC-2014, both Shimadzu Corp.) fitted with a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively. The columns in the FID-GC consisted of a Gaskuropack 55 (2 m  $\times$   $\Phi$  3 mm) for the detection of 2-PEN, 2-PAN, and 1-PAN at a column temperature of 393 K. The columns in the TCD-GC consisted of a Porapak Q (6 m  $\times$   $\Phi$  3 mm) for the detection of propane and propylene at a column temperature of 423 K. For the detection of H<sub>2</sub>, the column in the TCD-GC consisted of a Shin-carbon-ST (4 m  $\times$   $\Phi$  3 mm) with a column temperature of 313 K. The conversion, the selectivity and the yield were estimated on a carbon basis. Typical estimation equations for the conversion of 2-PEN together with the selectivity and the yield to a target product of propylene are given. In those equations, 2-PEN(P) and 2-PAN(P) were moles of 2-PEN and 2-PAN in the product gas, and 1-PAN, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>2</sub>H<sub>4</sub>, and CH<sub>4</sub> were moles of the corresponding products. Therefore, the contribution of carbon deposition was not reflected by those parameters in the present study.

## 3. Results and Discussion

To select a suitable loading of nickel, **Table 1** com-

$$\text{Conversion of 2-PEN} = \left[ 1 - \frac{3 \times 2\text{-PEN(P)}}{3 \times [2\text{-PEN(P)} + 2\text{-PAN(P)} + 1\text{-PAN} + \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8] + 2 \times \text{C}_2\text{H}_4 + \text{CH}_4} \right] \times 100$$

$$\text{Selectivity to propylene} = \left[ \frac{3 \times \text{C}_3\text{H}_6}{3 \times [2\text{-PEN(P)} + 2\text{-PAN(P)} + 1\text{-PAN} + \text{C}_3\text{H}_6 + \text{C}_3\text{H}_8] + 2 \times \text{C}_2\text{H}_4 + \text{CH}_4} \right] \times 100$$

$$\text{Yield of propylene} = [\text{Conversion of 2-PEN}] \times [\text{Selectivity to propylene}] / 100$$

compares the catalytic activity for reductive conversion of 2-PEN over 1.0 g of Ni( $x$ )/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $x = 5, 10, 15,$  and  $20\%$ ) at 473 K, with  $P(2\text{-PEN})$  of 8.8 kPa, and  $P(\text{H}_2)$  of 13.5 kPa. Under these conditions, 2-PAN and propylene were detected, whereas 1-PAN, methane, and propylene were not detected as by-products. Selectivities to propylene were between 81.3 % and 98.3 %, regardless of the time-on-stream (TOS). Therefore, these conditions might eliminate the need to separate propane and propylene. As shown in **Table 1**, the best yield of C<sub>3</sub>H<sub>6</sub> was detected on Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Therefore, Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was used in this study.

**Figure 1** shows the effect of the reaction temperature on the reductive conversion of 2-PEN on Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Increasing the reaction temperature from 473 to 623 K, improved the propylene yield from 18.8 to 59.4 % at 0.75 h on-stream. On the other hand, the selectivity to propylene was suppressed from 95.7 to 78.6 %. When the reaction temperature was further increased to 673 K, the conversion of 2-PEN was decreased and the selectivities to methane and ethylene increased, resulting in lower propylene yield. No propane was detected at any reaction temperature. As shown in **Fig. 1**, the selectivities to methane and eth-

ylene increased with the reaction temperature. Therefore, even if propane is produced at a high temperature, it is cracked to methane and ethylene, and propane cannot be detected<sup>9</sup>). The catalytic activity tends to decrease with time-on-stream and the yield of propylene was also inadequate. Therefore,  $P(\text{H}_2)$  was increased from 13.5 to 20.3 kPa, and the amount of catalyst was increased from 1.0 to 1.4 g for up to 4.25 h on-stream at 623 K.

**Figure 2** shows the effect of the catalyst amount and  $P(\text{H}_2)$  on the reductive conversion of 2-PEN on Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 623 K. Using 1 g of catalyst, an increase in  $P(\text{H}_2)$  from 13.5 to 20.3 kPa resulted in higher selectivity to propylene from 79.2 to 87.2 % and higher yield of propylene from 43.1 to 49.2 % at 0.25 h on-stream. Unfortunately, the catalytic activity decreased with time-on-stream. At 4.25 h on-stream, selectivity to propylene was 70.5 % and yield of propylene was 21.4 % at  $P(\text{H}_2)$  of 13.5 kPa, but 77.6 % and 25.6 % at 20.3 kPa, respectively. Using 1.4 g of catalyst, an increase in  $P(\text{H}_2)$  from 13.5 to 20.3 kPa improved the selectivity to propylene to 84.3 % at  $P(\text{H}_2)$  of 13.5 kPa and the yield of propylene was improved to 76.3 % at  $P(\text{H}_2)$  of 20.3 kPa, both at 0.25 h on-stream. Again, the catalytic activity decreased with time-on-stream. However, as clearly shown in **Fig. 2**, the catalytic activity decreased significantly at the beginning of time-on-stream, and remained relatively stable. Also, no propane formation was detected under the reaction conditions shown in **Fig. 2**.

XRD was used for the characterization of Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> before and after the reduction and the results appear in subsets (A) and (B) in **Fig. 3**, respectively. Furthermore, XRD patterns of the catalyst previously used for obtaining the results shown in **Fig. 1** at 473 K and 623 K are featured in subsets (A) and (B) in **Fig. 4**, respectively, and that in **Fig. 2** at  $W$  of 1.4 g and  $P(\text{H}_2)$

Table 1 Reductive Conversion of 2-PEN on Ni( $x$ )/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at 473 K

$x$ [%]	TOS [h]	Conv. [%]		Selectivity [%]		Yield [%]	
		2-PEN	2-PAN	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>
5	0.25	12.0	3.8	96.2	11.5		
	1.25	10.9	3.1	96.9	10.5		
10	0.25	15.0	4.3	95.7	14.3		
	1.25	18.7	1.7	98.3	18.3		
15	0.25	12.8	1.7	98.3	12.6		
	1.25	17.4	18.7	81.3	14.1		
20	0.25	14.6	5.5	94.5	13.8		
	1.25	17.2	3.6	95.8	16.5		

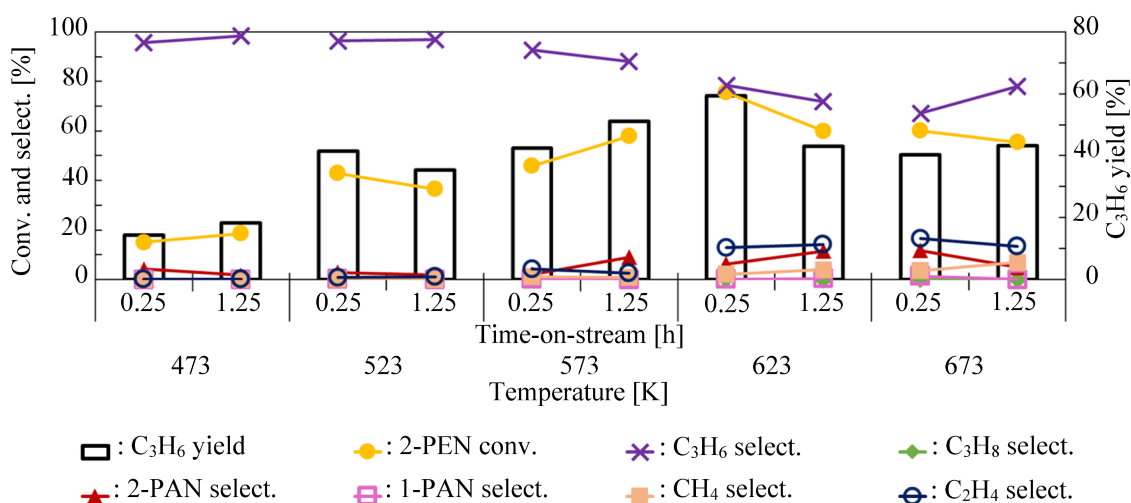


Fig. 1 Reductive Conversion of 2-PEN at Various Temperatures on Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

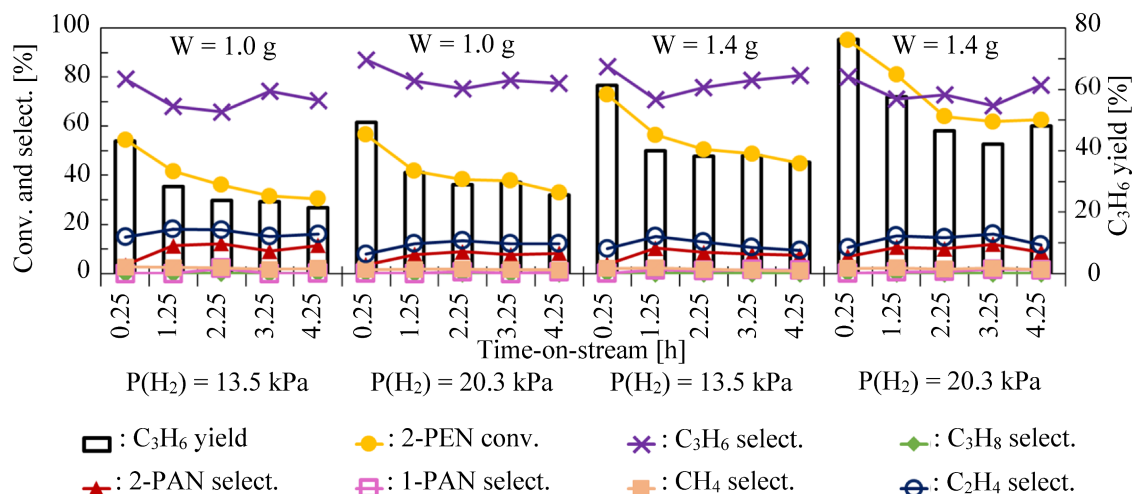


Fig. 2 Effects of the Catalyst Amount and  $P(\text{H}_2)$  on the Reductive Conversion of 2-PEN on  $\text{Ni}(10)/\gamma\text{-Al}_2\text{O}_3$

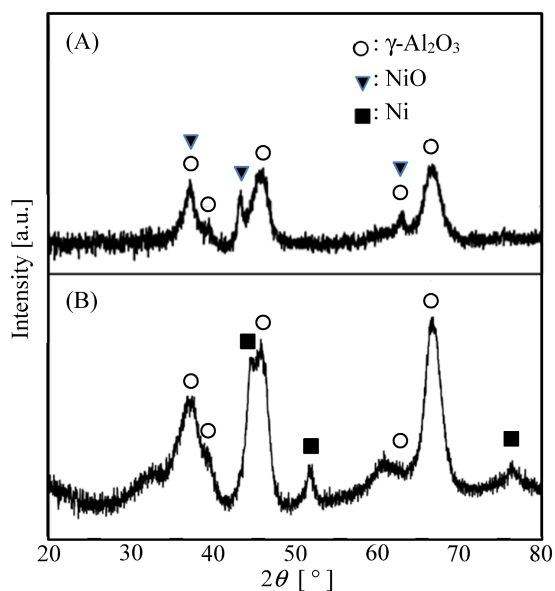


Fig. 3 XRD of  $\text{Ni}(10)/\gamma\text{-Al}_2\text{O}_3$  before (A) and after (B) the Reduction

of 20.3 kPa appeared in **Fig. 4(C)**. Comparing subsets (A) and (B) in **Fig. 3** confirmed that NiO (PDF 01-071-6719) on  $\gamma\text{-Al}_2\text{O}_3$  (PDF 00-050-0741) was reduced to metallic Ni (PDF 01-078-7536) by the reduction treatment employed in the present study.

Under the present reduction conditions, formation of  $\text{NiAl}_2\text{O}_4$  (PDF 01-078-6959) was possible. However, since the XRD peaks of  $\gamma\text{-Al}_2\text{O}_3$  and  $\text{NiAl}_2\text{O}_4$  overlap, the presence or absence of  $\text{NiAl}_2\text{O}_4$  is difficult to determine based on the results of XRD. However, since NiO and metallic Ni were clearly detected in subsets (A) and (B) in **Fig. 3**, respectively, any formation of  $\text{NiAl}_2\text{O}_4$  seemed to have little effect.

XRD patterns showed a clear conversion, particular-

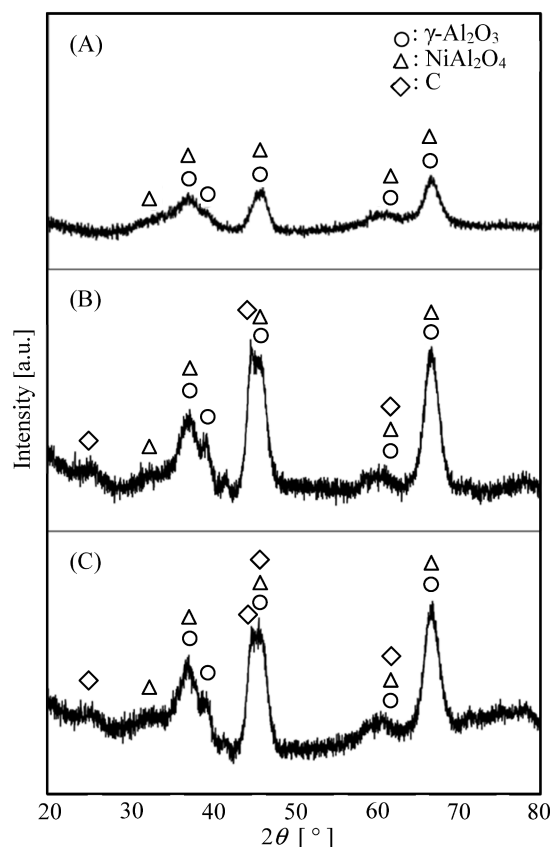


Fig. 4 XRD of  $\text{Ni}(10)/\gamma\text{-Al}_2\text{O}_3$  after Use to Obtain the Results Shown in Fig. 1 at (A) 473 K and (B) 623 K, Together with Fig. 2 at (C)  $W = 1.4$  g and  $P(\text{H}_2) = 20.3$  kPa

ly of the Ni species in the reaction on  $\text{Ni}(10)/\gamma\text{-Al}_2\text{O}_3$  shown in **Fig. 3(B)**. Subsets (A) and (B) in **Fig. 4** feature the XRD patterns of  $\text{Ni}(10)/\gamma\text{-Al}_2\text{O}_3$ , which gave the lowest and the highest yields of propylene at 473 K and 623 K, respectively, as shown in **Fig. 1**. As

Table 2 Carbon Deposition Rates per 1.0 g of Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Used to Obtain the Results Shown in Fig. 2

W [g]	$P(\text{H}_2)$ [kPa]	Carbon deposition rate per 1 g of Ni(10)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub> [g/g]
1.0	13.5	0.162
1.0	20.3	0.108
1.4	13.5	0.163
1.4	20.3	0.157

shown in subsets of (A) and (B) in Fig. 4, after use of the catalyst at 473 K and 623 K for 1.25 h on-stream (Fig. 1), the XRD signals due to metallic Ni had disappeared. This indicates the conversion of metallic Ni to NiAl<sub>2</sub>O<sub>4</sub>. Furthermore, the use at 623 K,  $W = 1.4$  g, and  $P(\text{H}_2) = 20.3$  kPa resulted in the formation of carbon (PDF 00-026-1080). The formation of NiAl<sub>2</sub>O<sub>4</sub> accompanying the disappearance of metallic Ni together with the detection of carbon was further clarified in Fig. 4(C). Since the catalyst shown in Fig. 4(C) provided the highest propylene yield (Fig. 2), formation of NiAl<sub>2</sub>O<sub>4</sub> in particular contributes greatly to the catalytic activity on Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Catalytic activity decreased with time-on-stream as shown in Fig. 2. Such a catalyst deterioration is influenced by carbon deposition and, in the present case, chlorine-poisoning. Therefore, thermogravimetric analysis was performed to quantify the amount of carbon deposition. Carbon deposition rates per 1.0 g of Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (CDR) previously used for obtaining the results shown in Fig. 2 are listed in Table 2.

Comparison of the values for CDR at  $W$  of 1.0 g and 1.4 g suggest the larger CDR is reasonable since the propylene yield was higher at  $W$  of 1.4 g than that at  $W$  of 1.0 g. In both cases, higher  $P(\text{H}_2)$  resulted in lower CDR, indicating that the presence of excess hydrogen suppresses carbon deposition. The amount of carbon deposition observed in the present study was approximately 1/10th that in the dehydrogenation of alkanes using the same catalyst<sup>12,13</sup>. Therefore, compared with the dehydrogenation of alkanes, in which carbon deposition drastically reduces the activity of the catalyst, the reductive dechlorination reaction of 2-PEN did not have a strong effect on catalyst deterioration due to carbon deposition.

The effect of chlorine-poisoning on Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was examined by XPS of the catalyst, which showed the highest activity at 623 K in Fig. 1. Figure 5(A) shows the results of XPS of Cl 2p on the surface of Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, both fresh and used for reaction at 623 K in Fig. 1, and Fig. 5(B) reveals that after argon ion sputtering, the Cl 2p signal was clearly detected from the unused catalyst due to chlorine-contamination in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Atomic ratios of Cl/Al before and after argon ion sputtering were 0.035 and 0.024, respectively,

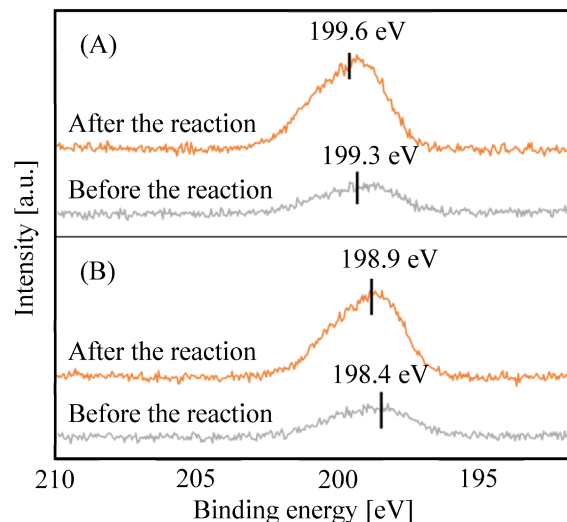


Fig. 5 XPS (A) before and (B) after Argon Ion Sputtering due to Cl 2p from Unused and Used Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

for fresh unused Ni(10)/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. After use for the reaction, the atomic ratios were increased to 0.071 and 0.066, respectively. Therefore, we concluded that chlorine-poisoning contributed to the catalyst deterioration as shown in Figs. 1 and 2.

### 3. Conclusions

We reported that  $\gamma$ -alumina-supported metallic palladium catalyst promoted nonselective conversion of 2-PEN<sup>6,7</sup>. However, the present study found that the  $\gamma$ -alumina-supported metallic nickel catalyst showed excellent activity for the selective dechlorination of 2-chloropropene to propylene. Decrease in catalyst activity was observed due to carbon deposition and chlorine poisoning at 2.25 h on-stream. However, the catalytic activity remained relatively stable from 2.25 to 4.25 h on-stream. Using the present catalyst system, no propane was observed, which eliminates the need for the difficult separation of propylene and propane in the refining process.

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### References

- 1) Miki, H., Izumi, Y., Oishi, T., Japanese Unexamined Patent Publication, No. S60-252434.
- 2) Miyazaki, H., Hasegawa, T., Japanese Unexamined Patent Publication, No. H6-135868.
- 3) Yano, M., Japanese Unexamined Patent Publication, No. 2007-332076.
- 4) Kinoshita, M., Omoto, N., Japanese Unexamined Patent Publication, No. 2011-105637.

- 5) Shimogama, S., Miyamura, S., Japanese Unexamined Patent Publication, No. 2013-100248.  
 6) Sugiyama, S., Fujimoto, R., Okita, C., Japanese Unexamined Patent Publication, No. 2020-21580.  
 7) Sugiyama, S., Endo, S., Noroyama, T., Hiwada, Y., Shimoda, N., *J. Jpn. Petrol. Inst.*, **64**, (4), 211 (2021).  
 8) Hirota, K., Hironaka, Y., *J. Catal.*, **4**, 602 (1965).  
 9) Hironaka, Y., Hirota, K., *Bull. Chem. Soc. Jpn.*, **38**, 1558 (1965).  
 10) Hirota, K., Hironaka, Y., *Bull. Chem. Soc. Jpn.*, **39**, 2638 (1966).  
 11) Thomson, G. W., *Chem. Rev.*, **38**, 1 (1946).  
 12) Sugiyama, S., Koizumi, A., Iwaki, T., Shimoda, N., Kato, Y., Ninomiya, W., *J. Chem. Eng. Jpn.*, **55**, 290 (2022).  
 13) Sugiyama, S., Yoshida, T., Shimoda, N., Ueki, T., Kato, Y., Ninomiya, W., *J. Chem. Eng. Jpn.*, **55**, 248 (2022).

## 要 旨

### アルミナ担持金属ニッケル触媒による2-クロロプロペンからプロピレンへの効果的な脱塩素

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前報では、アルミナ担持パラジウム触媒による2-クロロプロペン (2-PEN) の接触還元が348 Kで高い活性を示したことを報告した。しかしこの場合、2-クロロプロパン (2-PAN)、プロピレンおよびプロパンが非選択的に生成されたので、実際の社会実装を考えると分離プロセス併設が不可欠となっていた。本研究では、アルミナ担持ニッケル触媒が2-PENのプロピレンへの高選択的変換を達成できることを明らかにした。たとえば、473 Kでは、10%のNiを担持した触媒を用いると、2-PENの転化率が15.0%、プロピレンの選択率は95.7%に達

した。ただし、プロピレン収率が14.3%であったため、623 Kで反応を検討した。その結果、2-PENの転化率75.6%、プロピレンへの選択率78.6%となり、プロピレン収率が59.4%となった。最も注目すべき点は、この条件下でプロパンが生成されなかったことである。したがって、本触媒系では、プロパンとプロピレンを分離する必要はない。ニッケルを触媒として用いることで、プロピレンからプロパンへの過度の還元が抑制されると結論付けられた。