

[Regular Paper]

Synthesis of Chemical Precursors *via* the Catalytic Hydrogenation of 2-Chloropropene

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Allyl chloride, which is a cross-linking agent for synthetic resins and a synthetic intermediate that is used as an alkylating agent for pharmaceuticals, is often utilized and synthesized at production sites related organochlorides. In the synthesis process of allyl chloride, however, 2-chloropropene (2-PEN) is produced as the by-product and that is a problem because it essentially has no practical use. In this study, it was investigated about the hydrogenation of 2-PEN to 2-chloropropane (2-PAN) and propylene, which are precursors for various chemical products. The commercially available palladium catalysts such as OleMax 201, OleMax 301, OleMax 600, and HyFlex 500 were used for 2-PEN hydrogenation. The maximum yield of 2-PAN (10.6 %) was detected at 348 K, $P(\text{H}_2) = 13.5$ kPa and $P(2\text{-PEN}) = 8.8$ kPa, on OleMax 600 (0.5 g), while the maximum yield of propylene (26.0 %) was realized under the same reaction conditions, with the exception of using at $P(\text{H}_2) = 7.9$ kPa on HyFlex 500 (0.5 g). The selective formation of propylene such as 8.9, 100, and 8.9 % for the conversion of 2-PEN, the selectivity of propylene, and the yield of propylene, respectively, was realized on OleMax 201. The selective formation of 2-PAN, however, was not observed on all catalysts. Palladium loading strongly influenced the catalytic activity, but had none on either the specific surface area, or basic and acidic properties.

Keywords

2-Chloropropene, 2-Chloropropane, Propylene, Hydrogenation, Palladium catalyst

1. Introduction

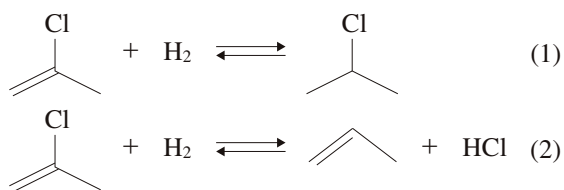
Since Japan is surrounded by the sea and is actively engaged in the petrochemical industry, the production of organochlorine compounds is thriving. Allyl chloride is one of the typical organochlorine compounds produced by the petrochemical industry. Allyl chloride has a wide range of uses such as a raw material for pharmaceuticals and agricultural chemicals, rubber products, various resin raw materials, and solvents, and is produced using propylene and chlorine as raw materials^{1)~5)}. Various organochlorine compounds are by-products of this production process^{1)~5)}. In this study, we focused on 2-chloropropene (2-PEN), which is one of the by-products in the process. 2-PEN can serve as a refrigerant, but has not been effectively used.

In the present study, we developed catalysts that would reduce 2-PEN in order to convert it to versatile materials such as 2-chloropropane (2-PAN) and propylene, the former of which is a raw material for thymol^{6)~8)} that is used to produce products ranging from daily necessities to pharmaceuticals^{9)~12)}. Needless to say, propylene is a key raw material for the petroleum industry. Therefore, if 2-PEN could be converted to 2-PAN and/or propylene, the added value of 2-PEN would be a welcome development. 2-PAN and propylene are produced from 2-PEN *via* hydrogenation (Eq. (1)) and hydrogenative dechlorination (Eq. (2)), respectively. As far as we could ascertain, no effective catalyst has been reported for either reaction. Therefore, in the present study, we focused on a palladium catalyst, which is a typical hydrogenation catalyst. We focused on a widely used commercially available alumina-supported palladium catalyst, and examined the selectivity of the two types of reduction reactions.

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2. Experimental

The catalytic experiments were performed in a fixed-bed continuous-flow quartz reactor at atmospheric pressure. 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 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 a mixture consisting of 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 equation¹³. The reactor was usually charged with an aliquot of 0.5 g. In all experiments, the temperature of the catalyst was raised to 473 K while maintaining a continuous flow of nitrogen. Then, pretreatment was performed for 0.5 h using hydrogen-containing gas obtained by removing 2-PEN from the raw gas used in the corresponding activity test at the reactor temperature. After the pretreatment, H₂ flow was stopped and the temperature was adjusted to a reaction temperature of 348 K. Then, a reactant gas mixture consisting of 2-PEN, H₂, and N₂ was introduced into the reactor at $P(2\text{-PEN}) = 8.8$ kPa, $P(\text{H}_2) = 2.3\text{--}27.0$ kPa, and $P(\text{N}_2) = 90.2\text{--}65.5$ kPa, respectively at a total flow rate of 90 mL/min. Under these conditions, homogeneous reactions were not detected. The reaction was monitored using two gas chromatographs (GC-8APT and GC-2014, both Shimadzu Corp.) that involved the use of a flame ionization detector (FID) and a thermal conductivity detector (TCD), respectively. The columns in the FID-GC consisted of a Gas-kuropack 55 (2 m × Φ 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 × Φ 3 mm) for the detection of propane and propylene at a column temperature of 423 K. For the detection of H₂, the column in the TCD-GC consisted of a Shincarbon-ST (4 m × Φ 3 mm) with a column temperature of 313 K. The conversion and the selectivity were estimated on a carbon basis. The hydrogen mass balance was also estimated on a hydrogen basis.

Four commercially available catalysts, OleMax 301, OleMax 201, OleMax 600, and HyFlex 500 (Clariant Catalysts (Japan) K.K.) were used in the present study. X-ray diffraction (XRD) patterns were measured using a SmartLab/R/INP/DX (Rigaku Corp.) with a Cu Kα radiation monochromator at 45 kV and 100 mA. The

Table 1 Pd Loading and Specific Surface Area of OleMax 301 (A), OleMax 201 (B), OleMax 600 (C), and HyFlex 500 (D), Respectively

| Catalyst | A | B | C | D |
|-------------------|------|------|-----|------|
| Pd ^{a)} | 0.03 | 0.03 | 0.3 | 0.77 |
| SSA ^{b)} | 227 | 32 | 109 | 35 |

a) Pd loading (wt%). b) Specific surface area (m²/g).

surfaces of the catalysts were analyzed using X-ray photoelectron spectroscopy (XPS; PHI-5000VersaProbe II, ULVAC-PHI Inc.). The XPS spectra of the catalysts were obtained using Al Kα radiation and were calibrated based on a C 1s peak at 284.6 eV. Argon ion sputtering was carried out at 2 kV for 2 min. The specific surface areas of those catalysts were estimated *via* nitrogen adsorption isotherms of the catalysts pretreated at 423 K under vacuum for 10 h using a BELSORP-max12 (MicrotracBEL Corp.) at 77 K. The acidic or basic properties of the catalysts were measured using either NH₃-temperature-programmed desorption (TPD) or CO₂-TPD, both in which the pretreatment temperature was adjusted to as 773 K. The desorbed NH₃ or CO₂ from the catalyst was monitored using a BELMass (MicrotracBEL Corp.) quadruple mass spectrometer with a mass signal of $m/e = 16$ or 44 for NH₃ or CO₂, respectively. It should be noted that when $m/e = 17$, this represented the mass signal of the NH₃ parent peak, which was strongly influenced by H₂O, and, thereafter, $m/e = 16$ was used for the analysis of NH₃.

3. Results and Discussion

3.1. Hydrogenation of 2-PEN to 2-PAN

Catalytic activity test was tested on 0.5 g each of OleMax 301, OleMax 201, OleMax 600, and HyFlex 500 with a mixture of gases consisting of 2-PEN and H₂ diluted with N₂ at 8.8 kPa and 7.9 kPa of $P(2\text{-PEN})$ and $P(\text{H}_2)$, respectively. The reaction temperature and the total flow rate was 348 K and 90 mL/min, respectively, for which no homogeneous reaction was detected. The rates of Pd loading and specific surface areas of OleMax 301, OleMax 201, OleMax 600, and HyFlex 500 were summarized in **Table 1**.

Figure 1 shows the catalytic activity during the hydrogenation of 2-PEN to 2-PAN on those four catalysts. On OleMax 301 and OleMax 201, 2-PAN was not produced at all probably due to a lower loading of Pd at 0.03 wt%. Raising the loading of Pd to 0.3 wt% resulted in an evident detection of 2-PAN that reached 2-PAN yield of 3.0 % after 1.25 h on-stream. A further increase of the loading of Pd to 0.77 wt%, however, decreased the yield of 2-PAN to 1.7 % after at 0.25 h on-stream. It is noteworthy that 99.0 % of C₃H₆ selectivity and 6.4 % of 2-PEN conversion after 0.25 h on-stream extensively changed 2-PAN selectivity to 100 %

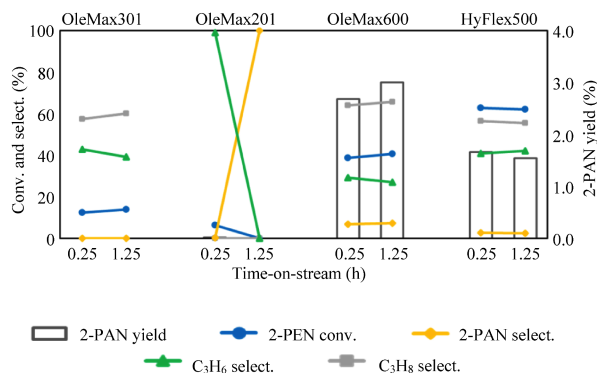
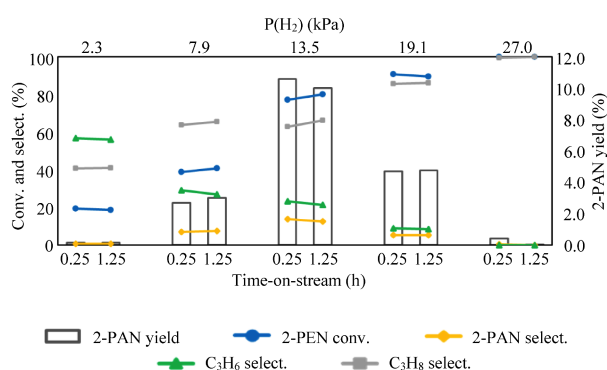


Fig. 1 Hydrogenation Activity on Each Catalyst

Fig. 2 Hydrogenation Activity on OleMax 600 with Various Amounts of $P(H_2)$

and almost 0.0 % of 2-PEN conversion after 1.25 h on-stream on OleMax 201. This indicates that, among the four catalysts, OleMax 201 was the most susceptible to the deactivation factors of the catalyst.

In order to enhance the 2-PAN yield, the effect of $P(H_2)$ during the hydrogenation of 2-PEN on OleMax 600 was examined. As shown in **Fig. 2**, with an increase of $P(H_2)$, both 2-PEN conversion and C_3H_8 selectivity were increased, while the selectivity for C_3H_6 was decreased, which resulted in the best 2-PAN selectivity with 2-PAN yield of 13.7 % and 10.6 %, respectively, after 0.25 h on-stream and $P(H_2) = 13.5$ kPa. As shown in **Fig. 2**, regardless of $P(H_2)$, since the selectivity for C_3H_6 was evidently greater than that for 2-PAN, we focus on the production of C_3H_6 in the following section.

3. 2. Hydrogenative Dechlorination of 2-PEN to C_3H_6

Figure 3 shows the catalytic activity for the hydrogenative dechlorination of 2-PEN to C_3H_6 on OleMax 301, OleMax 201, OleMax 600, and HyFlex 500 under the same reaction conditions with the exception of using $P(H_2) = 8.8$ kPa, as shown in **Fig. 1**. H_2 conversion is also described in **Fig. 3**. In the present reaction, it was necessary to actively dechlorinate and suppress the deep reduction of the produced propylene to

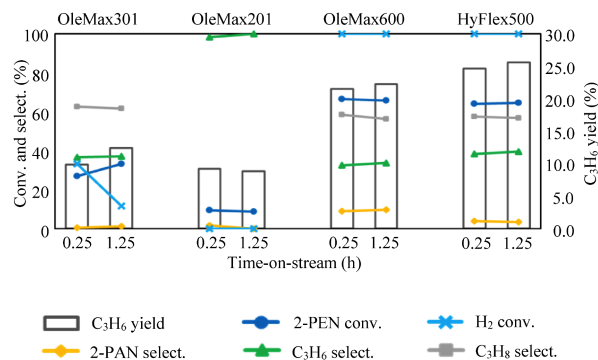


Fig. 3 Hydrogenative Dechlorination Activity on Each Catalyst

propane. Therefore, the present activity was tested using 2-PEN and an equimolar amount of H_2 .

As shown in **Fig. 3**, unlike the sequence of catalytic activity for the hydrogenation of 2-PEN to 2-PAN, which is shown in **Fig. 1**, HyFlex 500 gave the highest selectivity for, and yield of, C_3H_6 at 39.6 % and 25.6 %, respectively, after 1.25 h on-stream in the present hydrogenative dechlorination. Although the highest 2-PEN conversion was 66.5 % after 0.25 h on-stream on OleMax 600, C_3H_6 selectivity was about 5 % lower than that on HyFlex 500, which resulted in a second C_3H_6 yield of 22.3 % on OleMAX 600 after 1.25 h on-stream. Although the Pd loading was as low as 0.03 wt%, the formation of C_3H_6 was clearly detected on both OleMax 301 and OleMax 201 at 12.4 % and 8.9 % of the C_3H_6 yield on both catalysts, respectively, after 1.25 h on-stream. It should be noted that, unlike the results in **Fig. 1**, OleMax 201 showed stable activity within 1.25 h on-stream and C_3H_6 was produced with selectivity that approximately 100 % under conditions of almost 0 % of H_2 conversion. This indicates that the activation of H_2 seems to have difficulty proceeding on OleMax 201, which can be explained by a suppression of the deep reduction in the amount of propane produced by propylene.

Since HyFlex 500 showed superior activity for the hydrogenative dechlorination of 2-PEN to C_3H_6 , further examination of the effect of $P(H_2)$ on the reaction was observed, and the results appear in **Fig. 4**, together with the corresponding mass hydrogen balance in **Table 2**.

Figure 2 shows the results of the hydrogenation of 2-PEN to 2-PAN, wherein the yield of the target product (2-PAN yield) was significantly higher at a specific hydrogen partial pressure of $P(H_2) = 13.5$ kPa. With the hydrogenative dechlorination of 2-PEN to the target product (C_3H_6), however, a C_3H_6 yield exceeding 20 % was observed within a region of $P(H_2)$ ranging from 7.9 to 13.5 kPa, as shown in **Fig. 4**. The highest C_3H_6 yield was obtained at $P(H_2) = 7.9$ kPa, where 2-PEN conversion, C_3H_6 selectivity, and C_3H_6 yield were 61.9, 42.0, and 26.0 %, respectively, after 1.25 h on-stream.

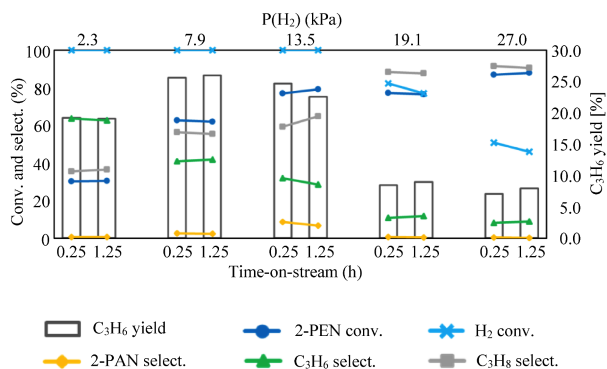


Fig. 4 Hydrogenative Dechlorination Activity on HyFlex 500 at Various Levels of $P(\text{H}_2)$

Table 2 Hydrogen Mass Balance (%) during the Reaction Described in Fig. 4

| TOS ^{a)} [h] | Partial pressure of hydrogen [kPa] | | | | |
|--------------------------|------------------------------------|-----|------|------|------|
| | 2.3 | 7.9 | 13.5 | 19.1 | 27.0 |
| 0.25 | 100 | 93 | 84 | 85 | 94 |
| 1.25 | 103 | 93 | 85 | 87 | 97 |

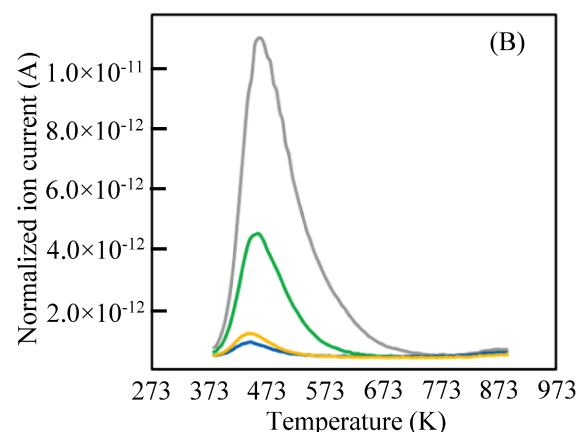
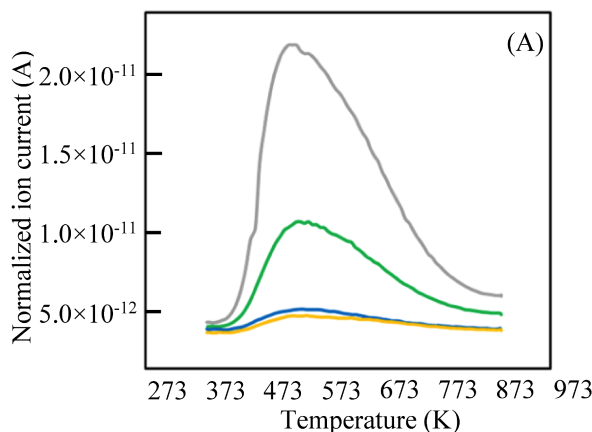
a) Time-on-stream.

When $P(\text{H}_2)$ was further increased, 2-PEN conversion was also increased, but the C_3H_6 yield was decreased due to a decrease in C_3H_6 selectivity and an increase in C_3H_8 selectivity. As shown in **Fig. 4**, the reaction proceeded under the hydrogen lean conditions at $P(\text{H}_2) = 13.5$ kPa and lower, while the hydrogen rich conditions at $P(\text{H}_2) = 19.1$ kPa and higher. As shown in **Table 2**, regardless to $P(\text{H}_2)$, the hydrogen mass balance was 84–103 % during the reaction, indicating that the consumed hydrogen was effectively used for the formation of products. The results of the present reaction revealed that $P(\text{H}_2)$ strongly contributes to the reductive process of 2-PEN to either 2-PAN or propylene together with a subsequent deep reduction to propane, which complicates the selective formation of target products such as 2-PAN or propylene.

3.3. Characterization of the Catalysts

The catalysts were characterized in order to investigate what properties contribute significantly to their catalytic activity. Based on XRD analyses of OleMax 301 and OleMax 600, $\gamma\text{-Al}_2\text{O}_3$ (PDF 00-047-1308) and $\eta\text{-Al}_2\text{O}_3$ (PDF 01-079-1557) were detected, while $\alpha\text{-Al}_2\text{O}_3$ (PDF 01-082-1467) and $\theta\text{-Al}_2\text{O}_3$ (PDF 00-023-1009) were detected from OleMax 201 and HyFlex 500. No XRD peaks based on Pd species appeared due to Pd species due to a small loading of the active species. Furthermore, there were no significant differences in the XRD patterns of those catalysts either before or after the reaction.

In order to estimate the relationship between the cat-



— OleMax301 — OleMax201
— OleMax600 — HyFlex500

Fig. 5 NH_3 -TPD (A) and CO_2 -TPD (B) of OleMax 301, OleMax 201, OleMax 600, and HyFlex 500

alytic activity and the acidic and basic properties, analyses using NH_3 -TPD and CO_2 -TPD were conducted for the four catalysts and the results are described in **Fig. 5(A)** and **5(B)**, respectively. Furthermore, the acidic and basic amounts estimated from **Fig. 5(A)** and **5(B)**, respectively, are summarized in **Table 3**. As shown in **Table 3**, the order of the acid amounts was OleMax 301 > OleMax 600 > OleMax 201 > HyFlex 500, while that of the base amounts was OleMax 301 > OleMax 600 > HyFlex 500 > OleMax 201. On the other hand, the order of hydrogenation activity from 2-PEN to 2-PAN was OleMax 600 > HyFlex 500 > OleMax 201 > OleMax 301, and that of hydrogenative dechlorination activity from 2-PEN to propylene was HyFlex 500 > OleMax 600 > OleMax 301 > OleMax 201. Therefore, the order of catalytic activity did not correlate with the acid-base properties of the four catalysts.

The results obtained using XRD and TPD strongly reflect the nature of the support rather than the catalytic active species of Pd. Therefore, the analysis was per-

Table 3 Acid and Base Amounts of OleMax 301, OleMax 201, OleMax 600, and HyFlex 500 Estimated Using NH_3 -TPD (A) and CO_2 -TPD (B)

| | Acid amount [mmol/g] | Peak top temp. for NH_3 -TPD [K] | Base amount [mmol/g] | Peak top temp. for CO_2 -TPD [K] |
|------------|-------------------------|--|-------------------------|--|
| OleMax 301 | 1.074 | 527.8 | 0.215 | 461.6 |
| OleMax 201 | 0.085 | 545.7 | 0.012 | 444.4 |
| OleMax 600 | 0.433 | 541.2 | 0.072 | 456.5 |
| HyFlex 500 | 0.072 | 552.4 | 0.020 | 443.7 |

formed *via* XPS, which can analyze even a small amount of Pd. In particular, OleMax 600 and HyFlex 500 were employed for the XPS analysis after showing the highest 2-PAN and C_3H_6 yields, respectively. **Figure 6(A)** and **6(B)** show the XPS spectra due to the Pd 3d of OleMax 600 and HyFlex 500, respectively, before and after the reaction at various levels of $P(\text{H}_2)$. From all of the samples, peaks due to Pd $3d_{3/2}$ and Pd $3d_{5/2}$ were detected as metallic Pd¹⁴. The peak due to Pd 3d from OleMAX 600 (**Fig. 6(A)**) shifted to the lower binding energy side following the reaction compared with that before the reaction, and the higher $P(\text{H}_2)$ used in the reaction resulted in a shift to the lower binding energy side. In contrast, the peak due to Pd 3d from HyFlex 500 (**Fig. 6(B)**) shifted to the higher binding energy side following the reaction compared with that before the reaction, and the higher $P(\text{H}_2)$ used in the reaction resulted in a shift to the higher binding energy side. Such a shift of the Pd 3d peak indicates that in the case of OleMax 600, Pd becomes anionic, while in the case of HyFlex 500, Pd becomes cationic with the reaction, both after the reaction at a higher levels of $P(\text{H}_2)$. In other words, Pd directly contributed to the reaction.

As shown in **Fig. 6**, the amount of metallic Pd on the surface of OleMax 600 and HyFlex 500 seemed to be considerably different. Furthermore, chlorinated species, which are expected to form *via* the dechlorination of 2-PEN, were certainly detected from all of the samples at 198.5–199.6 eV as a Cl 1s signal¹⁵. Therefore, the Pd and chlorine on the surfaces of OleMax 600 and HyFlex 500 were quantified *via* XPS, and the atomic ratio of each to the aluminum element appears in **Table 4**. The atomic ratios of Pd/Al on HyFlex 500 were evidently greater than those on OleMax 600, regardless of the usage and usage conditions. HyFlex 500 showed the best activity for the hydrogenative dechlorination to C_3H_6 and the second best for the dehydrogenation to 2-PAN. OleMax 600, on the contrary, showed the second best activity for hydrogenative dechlorination and the best activity for hydrogenation. Therefore, from the standpoint of hydrogenation, HyFlex 500 is a suitable catalyst. However, the amount of Pd both in and on the catalyst was so large that is enhanced the dechlorination. Therefore, OleMax 600 with the second highest loading of Pd seems to be the

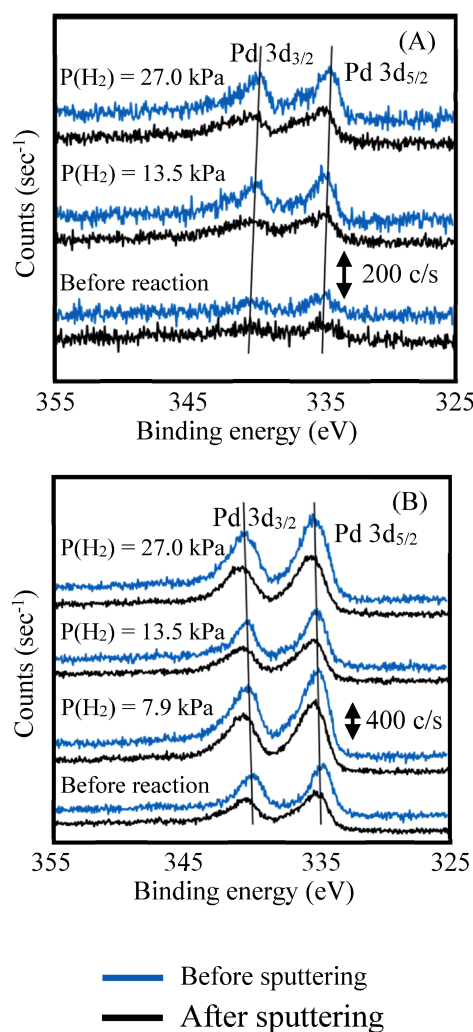


Fig. 6 XPS due to Pd 3d of OleMax 600 (A) and HyFlex 500 (B) before and after the Reaction at Various Levels of $P(\text{H}_2)$

best catalyst, from among the four tested, for obtaining 2-PAN. Although it is still in the preliminary experiment stage, a catalyst in which 0.77 % or more of Pd was supported on alumina was synthesized, and the effect of a Pd loading with a high loading rate on the reaction was verified. The effect of the high loading rate was not evidently detected yet. Additional study on the effect of Pd loading rate on activity is now in progress.

As shown in **Table 4**, OleMax 600 and HyFlex 500

Table 4 Atomic Ratio of Pd/Al and Cl/Al on the Near-surface Region of OleMax 600 and HyFlex 500 Estimated Using XPS

| Catalyst | Conditions | Sputtering | Pd/Al | Cl/Al |
|------------|---|-------------------|-------|-------|
| OleMax 600 | Before reaction | Before sputtering | 0.003 | 0.026 |
| | | After sputtering | 0.002 | 0.021 |
| | After reaction at $P(\text{H}_2) = 13.5$ kPa | Before sputtering | 0.006 | 0.030 |
| | | After sputtering | 0.004 | 0.054 |
| | After reaction at $P(\text{H}_2) = 27.0$ kPa | Before sputtering | 0.008 | 0.043 |
| | | After sputtering | 0.005 | 0.052 |
| HyFlex 500 | Before reaction | Before sputtering | 0.014 | 0.015 |
| | | After sputtering | 0.012 | 0.025 |
| | After reaction at $P(\text{H}_2) = 7.9$ kPa | Before sputtering | 0.027 | 0.037 |
| | | After sputtering | 0.020 | 0.040 |
| | After reaction at $P(\text{H}_2) = 13.5$ kPa | Before sputtering | 0.017 | 0.036 |
| | | After sputtering | 0.013 | 0.052 |
| | After reaction at $P(\text{H}_2) = 27.0$ kPa | Before sputtering | 0.024 | 0.023 |
| | | After sputtering | 0.016 | 0.040 |

contained chlorine, which was presumed to have been the results of their preparation using chlorine-containing raw materials. When used in the reaction, however, the amount of chlorine on the near-surface region of each catalyst was increased regardless of the usage conditions. Therefore, in order to carry out either the hydrogenation of 2-PEN to 2-PAN or the hydrogenative dechlorination of 2-PEN to C_3H_6 over a longer period of time, the contribution of the poisoning of the catalysts by chlorine should be considered.

4. Conclusions

Hydrogenation and hydrogenative dechlorination of chlorine-containing olefins, which are rarely studied, were investigated using four types of commercially available alumina-supported palladium catalysts. When 2-chloropropene was used as a raw material, the preparation of propylene *via* hydrogenative dechlorination was more advantageous than that of 2-chloropropane *via* hydrogenation. Catalytic activity proved to depend more on palladium loading than on the chemical properties of the catalyst.

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要 旨

2-クロロプロペンの接触水素化による化成品前駆体合成

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アクリクロライドは、医薬品のアルキル化剤や合成樹脂の架橋剤の原料として使用されるため、有機塩素化合物に関連する生産現場ではよく使用され、製造されている。しかし、このアクリクロライドの製造過程で、用途の少ない2-クロロプロペン (2-PEN) が副生し、問題となっている。本研究では、2-PEN の有効利用を目的として、2-PEN の接触水素化により、汎用性の高い化成品前駆体である2-クロロプロパン (2-PAN) とプロピレンの合成を検討した。また、触媒には OleMax 201, OleMax 301, OleMax 600, HyFlex 500 などの市販のパラジウム触媒を用いた。反応温度 348 K にて $P(\text{H}_2)=13.5 \text{ kPa}$ および $P(2\text{-PEN})=8.8 \text{ kPa}$ の反応条件下で、OleMax 600 (0.5 g) 触媒を

用いたときに2-PAN の収率 (10.6 %) が最大となった。一方、 $P(\text{H}_2)=7.9 \text{ kPa}$ とし、それ以外は同じ反応条件において、HyFlex 500 (0.5 g) 触媒を用いたときにプロピレンの収率 (26.0 %) は最大となった。OleMax 201 触媒を用いた場合、2-PEN の転化率、プロピレンの選択性、およびプロピレンの収率が、それぞれ 8.9, 100, 8.9 であった。このことから OleMax 201 触媒を用いることで、プロピレンが選択的に合成できることが明らかとなった。一方、2-PAN を選択的に合成する触媒は現在のところ見つかってはいない。触媒活性にはパラジウムの担持量は強く影響したが、比表面積や塩基性および酸性などの物性は触媒活性には影響しなかった。

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