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1,3-Butadiene Production by Crotyl Alcohol Dehydration over Solid Acids and Catalyst Deactivation by Water Adsorption

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We studied the synthesis of 1,3-butadiene via the dehydration of crotyl alcohol (2-buten-1-ol) over solid acids. Crotyl alcohol conversion and butadiene selectivity were both 95% or more over commercial silica-alumina catalysts. However, a sudden decrease in catalytic activity was observed during the reaction. On the basis of the fact that the deactivated catalyst was regenerated by drying at 150-200 °C, it was revealed that the main cause of the catalyst deactivation was the adsorption of water formed during the reaction and not the coke formation. An analysis of the deactivated catalyst indicated that, since the formation of Al-OH by the hydrolysis of the Al-O-Al bond increased the hydrophilicity of the catalyst surface, the adsorption of water on the catalyst surface was promoted, whereas that of crotyl alcohol was probably inhibited. Moreover, on the basis of the catalyst characterization, it was concluded that silica-alumina catalysts with few silanol groups, few alumina-rich zones, and a low Si/Al ratio were preferable.

Keywords
1,3-Butadiene, Alcohol dehydration, Silica-alumina catalyst, Catalyst regeneration, Water adsorption

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1. Introduction

1,3-Butadiene is an important chemical, of which 10 million tons per year are supplied to users worldwide
1). It is widely used in the production of synthetic rubbers and polymers, and polybutadiene rubber and styrene–butadiene rubber (SBR), the main products generated from butadiene, are crucial for tire production. The demand for butadiene is expected to rise with the constantly growing number of vehicles. Currently, about 95% of butadiene is obtained as a by-product of ethylene production using naphtha steam crackers. However, the rise of shale gas has prompted the replacement of naphtha as a feedstock by ethane, leading to lower butadiene production. The conversion of ethanol to butadiene can be separated into four steps
3,10,11), the last of which is the dehydration of crotyl alcohol.

Thus, in this report, we investigated the butadiene production by CA dehydration in order to complete the
four-step process.

Ichikawa et al. reported the synthesis of butadiene via C4-unsaturated alcohols from bio-based 1,3-butane-diol over solid acids\(^\text{17}\). In particular, 53 % crotyl alcohol conversion with 71 % butadiene selectivity was achieved over TiO\(_2\) at 375 °C, and the application of a silica-alumina catalyst at 250 °C afforded 77 % crotyl alcohol conversion with 93 % butadiene selectivity. Ochoa et al. employed SiO\(_2\)-MgO for crotyl alcohol dehydration and achieved 99.9 % crotyl alcohol conversion and 86 % butadiene yield at 400 °C\(^\text{18}\). Meanwhile, Sun et al. reported 99 % CA conversion with 97 % butadiene selectivity over a commercially available silica-alumina catalyst and 99 % crotyl alcohol conversion with 95 % butadiene selectivity over Ag/silica-alumina at 260 °C\(^\text{19}\). In that study, Ag/silica-alumina outperformed silica-alumina in terms of catalyst durability for crotyl alcohol dehydration, and it was demonstrated that catalyst deactivation was due to coke formation on the catalysts.

Our efforts focused on (1) revealing the causes of catalyst deactivation and developing an effective method of catalyst regeneration, and (2) determining the optimal characteristics of solid acids for the dehydration reaction.

2. Experimental

2.1. Solid Acids

Nine commercial catalysts —six silica-alumina catalysts (CAT-1 to CAT-6), two zeolite catalysts (CAT-7 and CAT-8), and one γ-alumina catalyst (CAT-9)— were supplied from Fuji Silysia Chemical Ltd., N. E. CHEMCAT Corp., Tosoh Corp., Sumitomo Chemical Co., Ltd., etc. All of the catalysts were pelleted to a size of 0.85-1.40 mm and dried at 130 °C for 12 h before the activity tests.

2.2. Activity Tests

Commercial crotyl alcohol (Aldrich, purity: 99 %, boiling point (Bp.): 121 °C) and supplied n-hexane (Wako Pure Chemicals Ind., Ltd., Japan, purity: > 96 %, Bp.: 69 °C) were used with no additional purification. The feeds were mixtures of crotyl alcohol and n-hexane (diluent). A tubular flow reactor loaded with 3 mL of catalyst was used for the activity tests. The reaction was carried out at 170-250 °C and ambient pressure in the gas phase. The liquid hourly space velocity of crotyl alcohol (LHSV-CA) was 0.75-1.5 h\(^{-1}\).

Product analysis was performed on an Agilent Technologies GC6850 gas chromatograph equipped with an Agilent 19091Z-436E HP-1 methyl siloxane capillary column (60.0 m long, 0.25 mm i.d., 0.25 μm film) and a flame ionization detector. A calibration plot was constructed for each product from commercially available standards. The reaction products were further identified by gas chromatography-mass spectrometry (GCMS). Crotyl alcohol conversion (mol%) and 1,3-butadiene selectivity (mol%) were determined using the following formulas:

\[
\text{Crotyl alcohol conversion (\%)} = \left(1 - \frac{\text{remaining crotyl alcohol (crotyl alcohol in feed)}}{\text{crotyl alcohol in feed}}\right) \times 100 \quad (1)
\]

\[
\text{Butadiene selectivity (\%)} = \frac{\text{butadiene yield (crotyl alcohol conversion)}}{\text{crotyl alcohol conversion}} \times 100 \quad (2)
\]

\[
\text{Butadiene yield (\%)} = \frac{\text{butadiene produced (crotyl alcohol in feed)}}{\text{crotyl alcohol in feed}} \times 100 \quad (3)
\]

The material balances calculated from the weight differences between the feeds and products were more than 98 %.

2.3. Characterization of Catalysts

Thermogravimetric (TG) analysis was conducted using Shimadzu DTG-60. The sample weight was around 15 mg, and the temperature was increased from room temperature to 600 °C at a rate of 10 °C/min. The weight loss between 300 °C and 600 °C under N\(_2\) flow was recorded to signify the burn-off of soft coke. The N\(_2\) flow was then switched to air for 10 min, and the weight loss during this period was measured to signify the burn-off of hard coke.

The acidic properties of the catalysts were investigated using infrared-mass (IRMS) spectroscopy combined with temperature-programmed desorption of adsorbed ammonia (NH\(_3\)-IRMS-TPD)\(^\text{20}\). After drying around 10 mg of a sample at 500 °C and adsorption of NH\(_3\) at 100 °C, IR and MS measurements were performed every 10 °C as the temperature was increased to 500 °C at a rate of 10 °C/min. The IR peaks at around 1264 cm\(^{-1}\) and 1465 cm\(^{-1}\) were assigned to the vibration of NH\(_3\) and NH\(_4^+\) on the Lewis and Bronsted acid sites, respectively. On the basis of the peak areas and NH\(_3\)-TPD profiles from the MS measurement, the amounts of Lewis and Bronsted acid sites were calculated\(^\text{21,22}\). The measurement of NH\(_3\)-IRMS-TPD was performed at Nissan Arc, Ltd.

The amounts of Al and Si in the catalysts were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) using a Hitachi High-Tech Science Corp. PS-3500 DDII.

\(^{29}\)Si and \(^{27}\)Al solid-state dipolar decoupling magic-angle spinning (MAS) nuclear magnetic resonance (NMR) experiments were performed at room temperature on a Varian NMR System 500 operating at a resonance frequency of 99.28 MHz for \(^{29}\)Si and 130.22 MHz for \(^{27}\)Al. The resonances of the NMR spectra were separated using MestReNova from Mestrelab Research S. L.

Temperature-programmed desorption mass spectroscopy of water (H\(_2\)O-TPD-MS) was performed on a Multitask TPD (MicrotracBEL Corp.) using a sample weight of 50-60 mg, and the temperature was increased from room temperature to 700 °C at a rate of 5 °C/min.
under He stream with a flow rate of 50 mL/min.

3. Results and Discussion

3.1. Dehydration of Crotyl Alcohol over CAT-1

The properties of the commercial solid acid catalysts (CAT-1 to CAT-9) are shown in Table 1. The specific surface areas of the six silica-alumina catalysts (CAT-1 to CAT-6) were similar, at around 400 m$^2$/g, and their SiO$_2$/Al$_2$O$_3$ ratios (mol/mol) ranged from 4 to 19.

Crotyl alcohol was fed with no diluent or inert gas over CAT-1 at an LHSV-CA of 1.0 h$^{-1}$. The composition of the reaction mixture after 20 min is shown in Fig. 1. Crotyl alcohol conversion was high (96 %), 1,3-butadiene selectivity was low (30 %), and a large quantity of by-products such as ethers and heavy products was detected. The possible routes of by-product formation over the silica-alumina catalysts are shown in Fig. 2. In this reaction, not only heavy products but also ethers, butenes, and alcohols were formed. 3-Buten-2-ol may have been formed through dehydration and subsequent hydration of crotyl alcohol, and the ethers may have been formed through the intermolecular dehydration of crotyl alcohol and 3-buten-2-ol.

To prevent this intermolecular dehydration, crotyl alcohol was diluted with n-hexane. The dilution’s effect on the catalytic performance is depicted in Fig. 3. The n-hexane/crotyl alcohol mixture was fed at an LHSV-CA of 1.3 h$^{-1}$ at 250 °C, and the n-hexane/crotyl alcohol (w/w) ratio varied from 2 to 9. Both crotyl alcohol conversion and butadiene selectivity increased as the ratio increased, and at ratios $\geq$ 5, they were over 95 %. The higher n-hexane/crotyl alcohol ratio led to an increase not only in butadiene selectivity but also in crotyl alcohol conversion, suggesting that the dilution contributed to the prevention of the intermolecular dehydration, thus favoring the intramolecular dehydration.

Consequently, it was found that high crotyl alcohol conversion and butadiene selectivity could be achieved simultaneously through proper control of the mixing ratio.

3.2. Screening of Commercial Solid Acids

To determine the suitable solid acids for crotyl alcohol dehydration, we performed activity tests with nine commercial solid acids, as shown in Table 1. The crotyl alcohol conversion and butadiene selectivity recordings in the initial stage of the reaction (20 min) and after 6 h are shown in Figs. 4 and 5, respectively.

On the basis of Fig. 4, the initial crotyl alcohol conversion and the initial butadiene selectivity in the case of the silica-alumina catalysts CAT-1 to CAT-6 were 100 % and around 90 %, respectively. However, CAT-4, CAT-5, and CAT-6 significantly decreased both the conversion and the selectivity after 6 h (Fig. 5). Meanwhile, the use of the two zeolites (CAT-7 and CAT-8) lowered the conversion and the selectivity compared to the silica-alumina catalysts, and the initial values were further diminished after 6 h. When the γ-alumina (CAT-9) was used, the initial conversion and selectivity were very low. Thus, the activity tests demonstrated that there are considerable differences among the investigated commercial solid acids.

As outlined in Table 1, the SiO$_2$/Al$_2$O$_3$ ratios of CAT-1 to CAT-3 were low (4-11), suggesting that cata-

![Table 1: Properties of Catalysts](image-url)
Catalysts with high numbers of acid sites are preferable for dehydration. Additionally, the catalysts with greater numbers of Brønsted acid sites (CAT-1 and CAT-5) showed higher catalytic activity than the catalyst having mostly Lewis acid sites (CAT-9). Hong et al. reported that higher isopropyl alcohol (IPA) conversion and propene selectivity were achieved with catalysts bearing a higher number of Brønsted sites\textsuperscript{23}. Furthermore, Sun et al. reported that a commercial silica-alumina catalyst was preferable to a commercial \( \gamma \)-alumina for crotyl alcohol dehydration\textsuperscript{19}. Thus, the presence of Brønsted acids on the catalysts is probably more favorable than that of Lewis acids.

Although the zeolites, namely, mordenite (CAT-7) and HZSM-5 (CAT-8), have Brønsted acid sites\textsuperscript{24}, they exhibited low crotyl alcohol conversion and butadiene selectivity, and significant catalyst deactivation. Since both catalysts had strong acid sites, the potential coke formation might have blocked the pores and resulted in catalyst deactivation.

Subsequently, it was found that the silica-alumina catalysts favor the crotyl alcohol dehydration compared to zeolites and \( \gamma \)-alumina. Among the six silica-alumina catalysts, CAT-1, CAT-2, and CAT-3 were better than CAT-4, CAT-5, and CAT-6. Moreover, since CAT-1 had the best catalytic performance, it was selected in the subsequent studies to investigate the catalyst deactivation factor and regeneration method.

3.3. Catalyst Deactivation and Regeneration

The effect of time-on-stream on crotyl alcohol conversion over CAT-1 under different reaction conditions is displayed in Fig. 6. The reactions were performed...
at 170 °C and 200 °C with mixing n-hexane/crotyl alcohol ratios of 5 w/w and 11 w/w. LHSV-CA was fixed at 0.75 h⁻¹. In each case, the crotyl alcohol conversion dropped suddenly after around 7 h, suggesting the catalyst deactivation. After 10 h, the amount of coke deposited on the catalysts was measured by TG analysis. The results are presented in Table 2. The amounts of coke were 30.6, 22.5, and 21.2 wt% when the reaction temperature and mixing n-hexane/crotyl alcohol ratio were 200 °C and 5 w/w, 200 °C and 11 w/w, and 170 °C and 11 w/w, respectively. Although the least amount of coke accumulated on the catalyst at 170 °C (21.2 wt%), a rapid catalyst deactivation was observed after 4 h, implying that it may be caused by something other than coke formation on the catalyst.

Table 2  Coke on CAT-1

| Reaction temp. [°C] | Feed ratio n-hexane/CA [w/w] | Coke on cat. (soft coke-hard coke) [wt%] |
|---------------------|-----------------------------|----------------------------------------|
| 200                 | 5                           | 30.6 (29.8-0.8)                        |
| 200                 | 11                          | 22.5 (21.8-0.7)                        |
| 170                 | 11                          | 21.2 (20.8-0.4)                        |

a) Crotyl alcohol.

Meanwhile, the effect of time-on-stream on selectivity in the reaction catalyzed by CAT-1 under different reaction conditions is illustrated in Fig. 7. In each case, butadiene selectivity decreased with the decrease in crotyl alcohol conversion, and 3-buten-2-ol was formed instead. After 7 h, phase-separated water was observed in the liquid reaction mixture because of dehydration, suggesting the effects of water adsorption. Once the catalytic activity decreased by water adsorption, dehydration was inhibited, and hydration was favored. Thus, the dehydration of crotyl alcohol and the subsequent hydration would proceed, leading to the formation of 3-buten-2-ol, thereby reducing the conversion.

Sun et al. studied the dehydration of crotyl alcohol over commercial silica-alumina catalysts and observed a sudden catalyst deactivation, as in the current study. They also demonstrated that the cause of deactivation was the coke accumulation on the catalyst. Their experiments were performed at 260 °C under a H₂-including atmosphere, whereas we used 170-200 °C and an inert gas (n-hexane). In their paper, the formation of 3-buten-2-ol was also not reported. Our experiments were performed at lower temperatures, which may have amplified the effects of water adsorption and led to the formation of 3-buten-2-ol, which can be considered as the evidence of the water adsorption effect on the catalyst.

The effect of catalyst drying on the catalytic performance was then explored. The reaction was performed at 200 °C with a n-hexane/crotyl alcohol feed ratio and a LHSV-CA of 5 w/w and 0.75 h⁻¹, respectively. The effect of drying the catalyst after the deactivation of CAT-1 is shown in Fig. 8. At 10 h, deactivation was observed, the feed was interrupted, and the catalyst was dried at 150 °C for 12 h in the air. After drying, crotyl alcohol conversion and butadiene selectivity recovered, and no 3-buten-2-ol formation was detected, suggesting that water adsorption might be the main cause of the catalyst deactivation. At 20 h, after the catalyst was deactivated for a second time, the catalyst
was dried again at 200 °C for 1 h under a N2 stream. The catalytic performance was restored again, indicating the catalyst drying as an effective way of catalyst regeneration. At 21 h, the amount of coke on the catalyst (soft coke: 28.0 wt%, calculated from the weight loss between 300 °C and 600 °C under N2 flow and hard coke: 0.6 wt%, calculated from the weight loss for 10 min at 600 °C under air flow) has not significantly changed compared to the amount at 10 h (30.6 wt%) (Table 2). The drying conditions at 10 h and 21 h were 150 °C for 12 h and 200 °C for 1 h, respectively, which were enough for sufficient catalyst regeneration. Consequently, despite the high coke accumulation, water adsorption was the main cause of catalyst deactivation. Since most of the coke was soft, it might move on the catalyst, implying that the catalyst active sites would not be always covered by coke.

The average composition of the reaction mixture obtained over the first 7 h of the experiment (Fig. 8) was also calculated. The average crotyl alcohol conversion and butadiene selectivity were 98 % and 94 %, respectively. By diluting crotyl alcohol, the ether selectivity was significantly reduced (0.1 %), and the selectivity values for 3-buten-2-ol, butenes, and heavy products (including C4 alcohols and aldehydes) were 0.8 %, 0.8 %, and 4.2 %, respectively. Hence, at lower temperatures, water adsorption had a greater effect than coke accumulation.

3.4 Behavior of Water on the Deactivated Catalyst

The 29Si solid-state MAS NMR experiments gave us insight into the silicon environment as the chemical shifts can specify the structural surroundings of the silicon atom. Tetrahedral silicon atoms are designated as Qn, where Q represents the SiO4 tetrahedron and n denotes the number of other tetrahedral silicon atoms linked to SiO4. The ratio of Q4 to all silicon atoms (Table 1) was calculated from three resonances at −92, −101, and −109 ppm, which were assigned to the Q2, Q3, and Q4 sites, respectively. Figure 9 shows the 29Si MAS NMR spectra of CAT-1 and the result of a deconvolution of the peaks attributed to Q2, Q3, and Q4.

Although the ratio of Q4 was calculated at 62 % (Table 1), it was difficult to distinguish Q3 from Si(1Al), a tetrahedral silicon atom with three −O−Si− bonds and one −O−Al− bond, and Q2 from Si(2Al), which is a tetrahedral silicon atom with two −O−Si− bonds and two −O−Al− bonds. The 29Si MAS NMR spectrum of CAT-1, deactivated after 5 h time-on-stream (reaction conditions: 170 °C, n-hexane/crotyl alcohol = 11, LHSV-CA = 1.5 h−1), was also compared with that of CAT-1 before the reaction (Fig. 9). The two spectra perfectly overlapped and hardly changed during the reaction.

In Fig. 10, the 27Al solid-state MAS NMR spectrum of the deactivated CAT-1 was compared with that of CAT-1 before the reaction. The spectrum consisted of three peaks at resonances of around 3, 29, and 57 ppm,
which were assigned to six-, five-, and four-coordinated Al, respectively.\(^{26-29}\) The two spectra almost overlapped, and they did not change during the reaction, similarly to the \(^{29}\)Si MAS NMR spectra.

In order to clarify the effect of water adsorption on CAT-1, H\(_2\)O-TPD-MS measurements were performed on CAT-1 before the reaction, after drying at 130 °C for 12 h, and after the reaction at 170 °C. The results are displayed in Fig. 11. Two water desorption peaks were detected before and after the reaction, whereas no lower desorption peak was observed for the catalyst dried at 130 °C. The lower temperature desorption peak was detected at around 50 °C before the reaction and at around 100 °C after the reaction. The elimination of this peak by drying at 130 °C before the reaction proved that it was mainly due to the desorption of physically adsorbed water. On the other hand, drying at 150-200 °C should eliminate the lower desorption peak observed after the reaction, suggesting that the water molecules associated with this peak play a major role in the catalytic activity decrease.

Meanwhile, after the reaction, the higher desorption peak shifted 50 °C higher (Fig. 11). This peak was probably due to water generated from the hydrolysis of the catalyst Si-O-Si, Si-O-Al, and Al-O-Al bonds during the reaction. Nevertheless, the \(^{29}\)Si and \(^{27}\)Al NMR spectra before and after the reaction did not differ. Therefore, the higher desorption peak after the reaction might be due to water produced mainly by the hydrolysis of the Al-O-Al bond, where Al atoms are six-coordinated, in alumina-rich zones\(^{30}\) of the catalyst. Furthermore, in contrast to the Si-O-Si bond, the Al-O-Al hydrolysis probably did not affect the \(^{29}\)Si and \(^{27}\)Al NMR spectra, and Si-O-Al should be hydrolyzed, similarly to Al-O-Al. However, given that the hydrolysis of Si-O-Al leads to a decrease in the number of Brønsted acid sites, the catalytic activity would not be recovered by drying at 150-200 °C. We therefore assumed that the hydrolysis of the Si-O-Al bond did not proceed further.

The higher desorption peak before the reaction could be attributed to water from the original OH groups of the catalyst, which seemed to desorb more easily than the water on the hydrolysate after the reaction at 170 °C that led to the 50 °C difference. It was thought that the Al-O-Al hydrolysis would not affect the catalytic activity, and in fact, the activity was restored by drying at 150-200 °C. Moreover, it appears that the easy adsorption of water on the hydrolysate of Al-O-Al after the reaction was stronger than the simple physical adsorption that occurs before the reaction, and drying at 150-200 °C resulted in the desorption of this water amount, thus explaining the shift of the lower desorption peak to 100 °C after the reaction.

On the basis of these experiments, in summary, it was demonstrated that, during the reaction, water formed on the acid sites of the catalyst and adsorbed easily, especially on the surface of the Al-O-Al hydrolysate in the alumina-rich zones, resulting in catalyst deactivation. Since the formation of Al-OH by the hydrolysis of Al-O-Al increased the hydrophilicity of the catalyst surface, the adsorption of water was promoted, and that of crotyl alcohol was inhibited.

### 3.5. Suitable Silica–alumina Catalysts

Silica–alumina catalysts with Q\(^4\) > 50 % are hydrophobic in nature because they contain few silanol groups, and it has been suggested that they do not readily adsorb the water formed during the reaction. Herein, the catalysts with a high Q\(^4\) percentage (CAT-1, CAT-2, and CAT-3) showed high activity after 6 h and displayed no deactivation tendency. Since the SiO\(_2/\)Al\(_2\)O\(_3\) ratios of CAT-5 and CAT-6 were low (SiO\(_2/\)Al\(_2\)O\(_3\) = 7 and 10, respectively), these catalysts seemed to be preferable for crotyl alcohol dehydration. They did, however, readily adsorb the generated water because of the low Q\(^4\) ratio (hydrophilicity), which led to catalyst deactivation.

It was thus concluded that suitable silica–alumina catalysts should have low Si/Al ratio (under 11) and high Q\(^4\) ratio (over 50 %) that lead to the increase of Brønsted acid sites and the decrease of silanol groups (hydrophobicity), respectively. It was also demonstrated that the catalysts meeting these criteria, i.e., CAT-1, CAT-2, and CAT-3, simultaneously exhibited high crotyl alcohol conversion and butadiene selectivity.

CAT-1 was the suitable dehydration catalyst because its Q\(^4\) ratio was around 62 % and it exhibited high hydrophobicity. As the reaction progressed, the hydrophilicity of the catalyst surface increased because of the adsorption of water on Al-OH, generated by the hydrolysis of the Al-O-Al bond, whereas crotyl alcohol adsorption was inhibited, thus decreasing the catalytic activity.

On the basis of the \(^{27}\)Al MAS NMR spectrum of Fig. 10, the amount of four-coordinated Al at around 57 ppm, which creates the Brønsted acid sites of silica-alumina, was not so high in CAT-1. Instead, the number of six-coordinated Al (about 3 ppm) was increased.
suggesting its presence in the Al-O-Al bonds in the alumina-rich zones. In addition to the limited Brønsted acid sites, CAT-1 was characterized by few silanol groups but an alumina-rich zone, which probably led to catalyst deactivation. Hence, an ideal solid acid for crotyl alcohol dehydration would be a silica-alumina catalyst with a high quantity of Brønsted acid sites, few silanol groups, and few alumina-rich zones. The application of such a catalyst will be investigated in our next research study.

4. Conclusions

The production of 1,3-butadiene by crotyl alcohol dehydration was investigated. Dilution of crotyl alcohol with n-hexane led to the reduction of intermolecular dehydration, and crotyl alcohol conversion and butadiene selectivity were both over 95 % in the early stages of the reaction over the commercial silica-alumina catalysts CAT-1, CAT-2, and CAT-3. Furthermore, a sudden catalyst deactivation was detected, and it was found that the catalyst could be regenerated by drying at 150-200 °C. It was thus suggested that water adsorption, and not coke formation, on the catalyst surface led to catalyst deactivation. The results of H2O-TPD, 29Si NMR, and 27Al NMR measurements implied that the adsorption of crotyl alcohol on the catalyst surface was inhibited, since the formation of Al-OH by the hydrolysis of Al-O-Al, where the Al atoms were six-coordinated, increased the hydrophilicity of the catalyst surface and the adsorption of water was promoted.

It was therefore demonstrated that silica-alumina catalysts with few silanol groups, few alumina-rich zones (hydrophobic), and a low Si/Al ratio (under 11) would favor crotyl alcohol dehydration.

References

1) Farzad, S., Mandegari, M. A., Görgens, J. F., Bioresour. Technol., 239, 37 (2017).
2) Angelici, C., Weckhuysen, B. M., Bruininx, P. C. A., ChemSusChem, 6, 1595 (2013).
3) Sushkevich, V. L., Ivanova, I. I., Ordomsky, V. V., Taarning, E., ChemSusChem, 7, 2527 (2014).
4) Sushkevich, V. L., Ivanova, I. I., Appl. Catal. B: Environ., 215, 36 (2017).
5) Maki-Arvela, P., Hajek, J., Salmi, T., Murzin, D. Y., Appl. Catal. A: Gen., 292, 1 (2005).
6) Axpucu, S., Aramendía, M. A., Hidalgo-Carrillo, J., Marinas, A., Marinas, J. M., Montes-Jiménez, V., Urbano, F. J., Borau, V., Catal. Today, 187, 183 (2012).
7) Corson, B. B., Jones, H. E., Welling, C. E., Hinckley, J. A., Stahly, E. E., Ind. Eng. Chem., 42, 359 (1950).
8) Corson, B. B., Stahly, E. E., Jones, H. E., Bishop, H. D., Ind. Eng. Chem., 41, 1012 (1949).
9) Duan, H., Yamada, Y., Sato, S., Chem. Lett., 45, 1036 (2016).
10) Niiyama, H., Morii, S., Echigoya, E., Bull. Chem. Soc. Jpn., 45, 655 (1972).
11) Jones, M. D., Keir, C. G., Julio, C. D., Robertson, R. A. M., Williams, C. V., Apperley, D. C., Catal. Sci. Technol., 1, 267 (2011).
12) Segawa, A., Nakashima, A., Nojima, R., Yoshida, N., Okamoto, M., Ind. Eng. Chem. Res., 57, 11852 (2018).
13) Horn, O., Ind. Eng. Chem., 51, 655 (1959).
14) Alheritiere, L., U.S. Pat. 2499608 (1949).
15) Takata, T., Nozawa, R., J. Synth. Org. Chem. Jpn., 33, 756 (1975).
16) Segawa, A., Taniya, K., Ichihashi, Y., Nishiyama, S., Yoshida, N., Okamoto, M., Ind. Eng. Chem. Res., 57, 70 (2018).
17) Ichikawa, N., Sato, S., Takahashi, R., Sodesawa, T., J. Mol. Catal. A: Chem., 256, 106 (2006).
18) Ochoa, J. V., Bandinelli, C., Vozniuk, O., Chieregato, A., Malmusi, A., Recchi, C., Cavani, F., Green Chem., 18, 1653 (2016).
19) Sun, D., Arai, S., Duan, H., Yamada, Y., Sato, S., Appl. Catal. A: Gen., 531, 21 (2017).
20) Niwa, M., Suzuki, K., Katada, N., Kanougi, T., Atochichi, T., J. Phys. Chem. B, 109, 18749 (2005).
21) Segawa, A., Taniya, K., Ichihashi, Y., Nishiyama, S., Yoshida, N., Okamoto, M., Ind. Eng. Chem. Res., 57, 70 (2018).
22) Sun, D., Yamada, Y., Sato, S., Suganuma, S., Katada, N., Appl. Catal. A: Gen., 526, 164 (2016).
23) Hong, E., Sim, H. I., Shin, C. H., Chem. Eng. J., 292, 156 (2016).
24) Nash, C. P., Ramanathan, A., Ruddy, D. A., Behl, M., Gjersing, E., Griffin, M., Zhu, H., Subramaniam, B., Schadie, J. A., Hensley, J. E., Appl. Catal. A: Gen., 510, 110 (2016).
25) Brunet, F., Charpentier, T., Caer, S. L., Renault, J.-P., Solid State Nucl. Magn. Reson., 33, 1 (2008).
26) Kim, Y. T., Jung, K. D., Park, E. D., Appl. Catal. B: Environ., 107, 177 (2011).
27) Hensen, E. J. M., Pudoval, D. G., Magusin, P. C. M. M., Coumans, A. E., Veen, J. A. R., J. Catal., 269, 201 (2010).
28) Murdkhe, K., Keyvanloo, K., Bartholomew, C. H., Hecker, W. C., Alam, T. M., Woodfield, B. F., Appl. Catal. A: Gen., 482, 16 (2014).
29) Parker Jr., W. O., Wegner, S., Micropor. Mesopor. Mater., 158, 235 (2012).
30) Hensen, E. J. M., Pudoval, D. G., Degirmenci, V., Ligthart, D. A. J. M., Chen, W., Maugé, F., Rigutto, M. S., Veen, J. A. R. v., J. Phys. Chem. C, 116, 21416 (2012).
要　旨
クロチルアルコール脱水による1,3-ブタジエン製造と水吸着による触媒活性低下

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固体酸触媒を用いて、クロチルアルコール（2-ブテン-1-オール）の脱水による1,3-ブタジエン製造を検討した。市販のシリカルミナにより、クロチルアルコール転化率とブタジエン選択率がともに95％に達したものの、急激な触媒活性低下が観測された。活性低下した触媒は150〜200℃という低温処理で再生できることから、触媒劣化の原因はコーキ生成というより反応中に生成した水の吸着によると思われる。活性低下した触媒の分析から、Al-O-Alの加水分解でのAl-OH形成により、触媒表面の親水性が高まり、水吸着が促進され、結果としてクロチルアルコールの吸着が阻害されたと考察した。触媒のキャラクタリゼーションから、この反応にはシラノール基およびアルミナ領域が少なく、Si/Al比の低いシリカルミナが好ましいことが分かった。