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Supported Ga-oxide Catalyst for Dehydrogenation of Ethane

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We studied dehydrogenation catalysts to improve the performance of the ethane cracking tube. Ga, Ge, In, and Sn were studied as dehydrogenation catalysts. Catalytic activity tests showed that the Ga catalyst has the best performance among them. Although the Ga catalyst supported on α -Al₂O₃ calcined at 1323 K deactivated with time on stream, the Ga catalyst supported on γ -Al₂O₃ calcined at 1323 K showed high ethylene yield and stability. Analyses of BET, XRD, EDX, and XANES were conducted to elucidate the differences of their performances. Ga catalyst supported on γ -Al₂O₃ calcined at 1323 K showed high catalytic activity and stability because Ga was supported as a highly dispersed β -Ga₂O₃-like structure thanks to high specific surface area of the γ -Al₂O₃ support.

Keywords

Ethane cracker, Ethane dehydrogenation, Gallium catalyst, XANES, Calcination temperature

1. Introduction

Industrially, ethylene is produced by steam cracking: naphtha and water vapor are supplied through a cracking coil heated to 973–1173 K, where naphtha is thermally decomposed in the gas phase. However, because of the recent shale revolution, ethylene production has shifted to ethane cracking, which is superior to naphtha cracking in terms of cost^{1),2)}.

Although the method is capable of producing large amounts of ethylene at low cost, there are various difficulties such as large energy consumption, decreased ethylene selectivity attributable to carbon deposition, and formation of by-products such as CH₄, CO, and CO₂^{3)~6)}. Therefore, it is necessary to develop a high-performance cracking coil capable of alleviating the shortcomings. AFTALLOY (Kubota Corp.), the latest cracking coil, has excellent ability to suppress carbon deposition and carburization compared with conventionally used cracking coils because the inner surface of the coil is covered with α -Al₂O₃. To improve the per-

formance of AFTALLOY further, coating a dehydrogenation catalyst on the coil to lower the reaction temperature is proposed in this study. The catalyst would be supported on the inner surface of the cracking coil to avoid pressure loss.

Many researchers have reported alkane dehydrogenation catalysts such as Cr, V, Ga, Mo and Pt^{7)~24)}. Especially, Cr and Ga catalysts have been reported because of their low-cost and high-performance. Regarding Cr catalyst, Hakuli *et al.* reported that 14–16 wt% CrO_x/Al₂O₃ showed high selectivity on dehydrogenation of isobutane and longer catalyst life¹²⁾. Shi *et al.* reported that 5 wt% Cr–10 wt% Ce/SBA-15 catalysts are effective for oxidative dehydrogenation of ethane and exhibited high conversion and ethylene selectivity¹³⁾. On the other hand, Ga is known to have high catalytic activity in dehydrogenation and oxidative dehydrogenation of propane. Zheng *et al.* reported that β -Ga₂O₃ exhibited the highest catalytic activity among the polymorphs of Ga₂O₃ because of the highest surface acid site density¹⁸⁾. They also reported that the surface acidity of the gallium oxides was related to the presence of Ga(IV) ions. Various supported-Ga catalysts have been also studied. For instance, Saito *et al.* reported that 1.7 wt% Ga/SiO₂ was effective for dehydrogenation of propane and demonstrated that the amount of carbonaceous deposits on the catalyst during dehydrogenation was around 1/10 in comparison with a silica-supported chromium oxide catalyst¹⁹⁾. In addition, Shen *et al.* reported that a Ga catalyst supported

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on a zeolite such as H-ZSM-5 was effective for dehydrogenation of ethane in the presence of CO_2 ²⁰⁾. The catalyst had high selectivity and long lifetime with increasing the Si/Al ratio because the acidity of the catalyst decreased. Moreover, not only supported catalysts but also solid solution catalysts have been reported on Ga catalysts. Chen *et al.* reported that $\text{Ga}_8\text{Al}_2\text{O}_{15}$ synthesized with a co-precipitation method exhibited high propane conversion and selectivity. They postulated that the amount of tetrahedral surface Ga^{3+} was important for the catalytic activity²¹⁾.

This study investigated Ga and other elements including Ge, In and Sn, which are located near gallium in the periodic table, to assess their catalytic activities for dehydrogenation of ethane. Because the $\gamma\text{-Al}_2\text{O}_3$ supported Ga catalyst calcined at 1323 K showed high catalytic activity and stability, we investigated the structure and the role of Ga using BET, XRD, TEM-EDX, and XAFS measurements.

2. Experimental

2.1. Catalyst Preparation

Using a planetary ball mill (P-6; Fritsch GmbH), $\gamma\text{-Al}_2\text{O}_3$ (JRC-ALO-6; Catalyst Society of Japan) was crushed into particles. The $\gamma\text{-Al}_2\text{O}_3$ powder was used as the catalyst support or calcined in air at 1573 K for 3 h to be $\alpha\text{-Al}_2\text{O}_3$. Ga, Ge, In, or Sn was loaded on the support with an impregnation method. The catalyst support was soaked in distilled water for 2 h. Then an aqueous solution of $\text{Ga}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ($n = 7\text{--}9$), $\text{In}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$, GeCl_2 or $\text{Sn}(\text{CH}_3\text{COO})_2$ was added. After the slurry was stirred at room temperature for 2 h, water was evaporated with heating and stirring. Then, the obtained powder was dried in an oven at 393 K overnight in air and was calcined in a muffle furnace at 1323 K or 1573 K for 3 h in air.

In this paper, catalysts are denoted as M- Al_2O_3 (1573pc + xc). Here, M means the supported metal. We describe the calcination conditions in the parenthesis. The pre-calcination (pc) condition before loading active metal is shown in case of $\alpha\text{-Al}_2\text{O}_3$ as a support, because $\alpha\text{-Al}_2\text{O}_3$ was obtained by the calcination of $\gamma\text{-Al}_2\text{O}_3$ at 1573 K before impregnation. Then, the metal-impregnated catalyst was calcined at 1323 K or 1573 K, the temperature is denoted as x in the parenthesis. No expression for the pre-calcination condition is shown when $\gamma\text{-Al}_2\text{O}_3$ was used for impregnation.

2.2. Catalytic Activity Test

Catalytic activity tests were conducted in a fixed bed flow quartz tube reactor (4 mm i.d./6 mm o.d.) under atmospheric pressure. The catalyst (100 mg) was sieved to 355–500 μm particles and was charged into the reactor with SiC (392 mg) so that the catalyst bed height was 30 mm. The furnace was heated to 973 K excluding a part of sections 3.1.2. and 3.1.3. at a ramping

rate of 40 K min^{-1} . N_2 was used as a diluted gas. The reaction gas composition was $\text{C}_2\text{H}_6 : \text{H}_2\text{O} : \text{N}_2 = 1 : 1.36 : 5.41$, with a total flow rate of 281.6 SCCM (SATP) except for a part of section 3.1.2. For the products analysis, reaction tube was connected to a gas chromatograph: a GC-FID (GC-8A) with a Porapak Q packed column and a methanizer (Ru/ Al_2O_3 catalyst). Ethane conversion and ethylene selectivity were calculated by the following equation.

$$X_{\text{C}_2\text{H}_6} [\%] = \frac{r_{\text{CO}} + r_{\text{CH}_4} + r_{\text{CO}_2} + 2 \times r_{\text{C}_2\text{H}_4}}{2 \times f_{\text{C}_2\text{H}_6}} \times 100$$

$$S_{\text{C}_2\text{H}_4} [\%] = \frac{r_{\text{C}_2\text{H}_4}}{r_{\text{CO}} + r_{\text{CH}_4} + r_{\text{CO}_2} + r_{\text{C}_2\text{H}_4}} \times 100$$

Here, $X_{\text{C}_2\text{H}_6}$ represents ethane conversion and r indicates the formation rate of each product (CO, CH_4 , CO_2 and C_2H_4) described by the subscripts. Ethane feed rate is denoted as $f_{\text{C}_2\text{H}_6}$, and $S_{\text{C}_2\text{H}_4}$ means ethylene selectivity. No other product was detected. Therefore, $X_{\text{C}_2\text{H}_6}$ and $S_{\text{C}_2\text{H}_4}$ are the calculated value on the basis of the carbon amount of the converted ethane.

2.3. Catalyst Characterization

The crystalline structure was characterized by an X-ray diffractometer (Smart Lab-III; Rigaku Corp.) operated at 40 kV and 40 mA using Cu- $K\alpha$ radiation. The specific surface area of the catalyst was measured by N_2 adsorption using Brunauer-Emmett-Teller method (BET, Gemini VII; Micromeritics Instrument Corp.). The dispersion of Ga on the catalyst was estimated by a transmission electron microscope with an energy dispersive X-ray spectrometer (JEM-2100; JEOL Ltd.). Mappings for O, Al, and Ga were also measured using energy dispersive X-ray spectroscopy (EDX).

The electronic state of Ga was investigated by X-ray absorption near-edge structure (XANES) for Ga K -edge at the BL14B2 station of SPring-8 in Japan. Before XANES measurements, the catalyst was crushed into particles using a planetary ball mill and was pressed into a pellet (7 mm ϕ disk). The pellet was diluted with BN to be suitable for XANES measurement.

2.4. Computational Method

Plane wave basis pseudopotential calculations were implemented in the CASTEP code²⁵⁾ to simulate the XANES spectra. The exchange correlation function was Perdew-Burke-Ernzerhof (PBE) out of the generalized gradient approximation (GGA). Ultrasoft pseudopotentials were used. The plane wave cutoff energy (E_{cut}) was taken as 630 eV. The k -point separation in the Monkhorst-Pack reciprocal space was set as approximately 0.07 $\text{\AA}^{-1}$ (1 $\text{\AA} = 10^{-10}$ m). For comparison with the experimental spectra, the theoretical spectra were broadened using Gaussian and Lorentzian parameters set respectively as 0.2 eV and 0.4 eV. Details of spectrum calculation are given in the literature²⁶⁾. In the pseudopotential method, the transition energy cannot be obtained in cases where only valence electrons are con-

(a) C_2H_4 -formation rate, (b) C_2H_4 selectivity.

Fig. 1 Screening Tests for Various Catalysts at 973 K

sidered in all energy. It is also necessary to evaluate the core electron contribution. Details of transition energy calculations were described in an earlier report²⁷.

3. Results

3.1. Dehydrogenation of Ethane

3.1.1. Screening Better Catalysts for Dehydrogenation of Ethane

Four chemical elements (Ga, Ge, In, and Sn) were tested to investigate their catalytic activities for dehydrogenation of ethane. The dehydrogenation reaction of ethane was conducted at 973 K. Considering the surface structure of AFTALLOY on which $\alpha\text{-Al}_2\text{O}_3$ is coated, 5 wt% Ga, Ge, In or Sn was impregnated on $\alpha\text{-Al}_2\text{O}_3$. Results of screening tests are presented in **Fig. 1**. These results indicate that $\text{Ga-Al}_2\text{O}_3$ (1573pc + 1323c) has a high ethylene formation rate and high ethylene selectivity. Although $\text{In-Al}_2\text{O}_3$ (1573pc + 1323c) exhibited a high ethylene formation rate, ethylene selectivity was about 70 %, which was lower than those on the other catalysts. $\text{Ge-Al}_2\text{O}_3$ (1573pc + 1323c) was slightly inferior to the Ga catalyst in terms of the ethylene formation rate and selectivity, but it showed high stability. Considering the price of Ge, it is not feasible for industrial use. The catalytic activity of $\text{Sn-Al}_2\text{O}_3$ (1573pc + 1323c) was almost identical to that of $\alpha\text{-Al}_2\text{O}_3$. Therefore, Sn has no catalytic activity for dehydrogenation of ethane. From the results presented above, we concluded that Ga is the most effective element for dehydrogenation of ethane under these reaction conditions.

3.1.2. Activity Tests by Changing Support or Calcination Temperature

To improve the dispersion of active sites (*i.e.* Ga) on $\text{Ga-Al}_2\text{O}_3$ (1573pc + 1323c), catalysts were prepared using $\gamma\text{-Al}_2\text{O}_3$ as a support, which has much higher specific surface area than $\alpha\text{-Al}_2\text{O}_3$. To ascertain whether Al-Ga solid solution is suitable or not for the purpose, the Ga catalysts supported on $\alpha\text{-Al}_2\text{O}_3$ or $\gamma\text{-Al}_2\text{O}_3$ were calcined at 1573 K to form the solid solution. Results are presented in **Fig. 2**. The ethylene formation rate tended to decrease irrespective of calcination temperature when $\alpha\text{-Al}_2\text{O}_3$ was used as a support. $\text{Ga-Al}_2\text{O}_3$ (1573pc + 1323c) exhibited higher ethylene formation rate than the catalyst calcined at 1573 K. On the other hand, high catalytic activity and stability were observed over $\text{Ga-Al}_2\text{O}_3$ (1323c). In the case of $\text{Ga-Al}_2\text{O}_3$ (1573c), the ethylene formation rate was low, but no decrease in catalytic activity was observed with time on stream. Although it is effective to use $\gamma\text{-Al}_2\text{O}_3$ as a support, no improvement could be observed over bare Al_2O_3 (1323c). The catalytic activity of Al_2O_3 (1323c) was the same level to that of Al_2O_3 (1573c). Therefore, it should be considered that Ga species is important for the active sites and the high specific surface area of the support is only important for the dispersion of Ga.

For $\text{Ga-Al}_2\text{O}_3$ (1573pc + 1323c), the ethylene formation rate rapidly decreased with time on stream. In this reaction system, carbon deposition, sintering of Ga, and poisoning by the strong adsorption of hydrocarbons are regarded as factors to lower the catalytic activity. Carbon deposition is negligible in this study as mentioned above. Here, to assess the possibility of poisoning by the strong adsorption of hydrocarbons, N_2

purging was conducted after the reaction, then, the ethylene formation rate was measured. Results are presented in **Table 1**. The catalytic activities of Ga-Al₂O₃ (1573pc + 1323c) and Ga-Al₂O₃ (1573pc + 1573c) were regenerated by N₂ purging. Therefore, deactivation over these catalysts might derive from the surface adsorption of hydrocarbons.

3. 1. 3. Evaluation of Apparent Activation Energy, Selectivity to Products and Activity Tests of Test Pieces

Ga-Al₂O₃ (1323c) showed better performance than the other catalysts in this work. To elucidate the causes of its high performance, catalytic activity tests were conducted at various temperatures (953-1033 K) for the Ga-Al₂O₃ (1323c) catalyst and α -Al₂O₃ (*i.e.* Al₂O₃ (1573c)) as a model of AFTALLOY to measure the apparent activation energy (E_a). Arrhenius plots for both catalysts are shown in **Fig. 3**. Based on the results, E_a of the gas phase reaction (*i.e.* on bare alumina without Ga) was 283.7 kJ mol⁻¹ and E_a of the surface reaction with Ga was 211.4 kJ mol⁻¹. These results show that coating Ga on the AFTALLOY can lower the reaction temperature drastically.

The ethane conversion and selectivity over the Ga-catalyst and gas phase reaction (*i.e.* over bare alumina without Ga) were compared at the same conversion level. Ethane conversion and ethylene yield were in proportion to the contact time (*i.e.* space velocity) over the Ga-Al₂O₃ (1323c) catalyst, and were much higher than that on gas phase reaction (bare alumina without Ga).

Fig. 2 Activity Tests for Various Ga-catalysts at 973 K

On the other hand, the selectivity to ethylene was 85 % on Ga-Al₂O₃ (1323c), and lower than that for gas phase reaction (95 %). From these results, Ga-Al₂O₃ (1323c) catalyst showed higher activity but further increase in selectivity to ethylene should be required.

Small test pieces were prepared by coating the catalyst on the model AFTALLOY piece to confirm the effect of the catalyst on the AFTALLOY surface. Results are depicted in **Fig. 4**. The test piece with Ga₂O₃ showed a higher ethylene formation rate than the model AFTALLOY. The high stability was also observed over the Ga₂O₃ loaded test piece. These results confirm that Ga₂O₃ has high catalytic activity even when it is loaded on a cracking coil.

3. 2. Structural Characterization

3. 2. 1. XRD and BET

To evaluate the high performance of the Ga-supported catalyst, X-ray diffraction (XRD) measurements were conducted for Ga-Al₂O₃ (1573pc + 1323c), Ga-Al₂O₃ (1573pc + 1573c), Ga-Al₂O₃ (1323c), and Ga-Al₂O₃ (1573c). Results are portrayed in **Fig. 5**. From the results, only Ga-Al₂O₃ (1323c) showed θ -Al₂O₃ structure. The others showed α -Al₂O₃ phase. Peaks for Ga were not detected because Ga species might exist on the catalyst with highly dispersed.

To evaluate the effects of the specific surface area of the support on the catalytic activity, we measured the

Fig. 3 Arrhenius Plots for Dehydrogenation of Ethane over Ga-Al₂O₃ (1323c) and Al₂O₃ (1573c)

Table 1 The Effect of N₂ Purge on the Catalytic Activities

Catalyst	Initial activity [mmol g ⁻¹ h ⁻¹]	Activity at 180 min [mmol g ⁻¹ h ⁻¹]	Initial activity after N ₂ purge [mmol g ⁻¹ h ⁻¹]
Ga-Al ₂ O ₃ (1573pc + 1573c)	5.97	5.56	5.91
Ga-Al ₂ O ₃ (1573pc + 1323c)	9.81	6.92	8.13

Fig. 4 Activity Tests over Test Pieces at 973 K

Fig. 5 XRD Patterns for Ga-Al₂O₃ (1323c), Ga-Al₂O₃ (1573pc + 1323c), Ga-Al₂O₃ (1573c) and Ga-Al₂O₃ (1573pc + 1573c)

BET surface area of the catalyst. Results of BET measurements for these catalysts are presented in **Table 2**. The BET surface area of Ga-Al₂O₃ (1323c) was 49.3 m² g⁻¹, which is 10 times higher than that of the other catalysts, by virtue of θ-Al₂O₃.

3. 2. 2. TEM-EDX

As presented in section 3. 1., Ga-Al₂O₃ (1323c) showed the high ethylene formation rate and stability, but the catalytic activity of Ga-Al₂O₃ (1573pc + 1323c), Ga-Al₂O₃ (1573pc + 1573c) decreased with time on stream. To identify the factors causing this difference in stability, high-angle annular dark field (HAADF) images and energy dispersive X-ray fluorescence spectrometer

Table 2 Specific Surface Area of Various Ga Catalysts

Catalyst	Specific surface area [m ² g ⁻¹]
Ga-Al ₂ O ₃ (1323c)	49.3
Ga-Al ₂ O ₃ (1573pc + 1323c)	5.5
Ga-Al ₂ O ₃ (1573c)	4.3
Ga-Al ₂ O ₃ (1573pc + 1573c)	4.4

Fig. 6 HAADF Images and EDX Mappings for (a) Ga-Al₂O₃ (1323c), Ga-Al₂O₃ (1573pc + 1323c), Ga-Al₂O₃ (1573c) and Ga-Al₂O₃ (1573pc + 1573c), (b) Ga-Al₂O₃ (1323c) and Ga-Al₂O₃ (1573pc + 1323c) after the Reaction at 973 K for 4.5 h

(EDX) mappings by field emission-transmission electron microscope (FE-TEM) were observed. **Figure 6(a)** presents HAADF images and EDX mappings of Ga-Al₂O₃ (1323c), Ga-Al₂O₃ (1573pc + 1323c), Ga-Al₂O₃ (1573c) and Ga-Al₂O₃ (1573pc + 1573c). As shown in **Fig. 6(a)**, Ga was agglomerated on Ga-Al₂O₃ (1573pc + 1323c), whereas Ga was highly dispersed on Ga-Al₂O₃ (1323c). No significant difference was observed in the dispersion of Ga even when the catalyst were calcined at 1573 K. Sintering was not observed by high temperature calcination. **Figure 6(b)** presents the results of HAADF and EDX of Ga-Al₂O₃ (1323c) and Ga-Al₂O₃ (1573pc + 1323c) after the reaction. In comparison with **Fig. 6(a)**, the

Fig. 7 XANES Spectra by (a), (c) Experiments and (b), (d) Calculations

dispersion of Ga did not change after the reaction in both cases.

3.2.3. XANES

To investigate the coordination environment and the electronic state of Ga species on Ga-Al₂O₃ (xc) catalysts, Ga *K*-edge XANES spectra were measured. **Figure 7(a)**-Exp. depicts experimental Ga *K*-edge XANES spectra for Ga-Al₂O₃ (1323c), Ga-Al₂O₃ (1573c) and reference samples of β -Ga₂O₃ and α -Ga₂O₃. **Figure 7(b)**-Calc. portrays the calculated spectra for α -Ga₂O₃, β -Ga₂O₃, α -Ga₂O₃ (Al-rep), and β -Ga₂O₃ (Al-rep) with *ab initio* calculations. The description (Al-rep) shows the replacement of some Ga ions with Al ions. Comparing the experimental spectra with the calculated ones, the peak position of Ga-Al₂O₃ (1323c) was similar to that of the calculated spectrum of β -Ga₂O₃. However, the peak intensity of the low transition energy (10373 eV) is higher than that of the high transition energy (10378 eV)²⁸. It is known that β -Ga₂O₃ is the only stable phase²⁹ and it includes two kinds of Ga, tetrahedral Ga and octahedral Ga, in its structure³⁰. Thus, we calculated spectra of tetrahedral Ga and octahedral Ga shown in **Fig. 7(b)** because we

suppose that the difference between the experimental and theoretical spectra derive from the coordination environment of Ga. As shown in **Fig. 7(b)**, tetrahedral Ga in β -Ga₂O₃ showed relatively low peak position (10413 eV). Therefore, it is considered that the amount of tetrahedral Ga is larger than that of octahedral Ga in the Ga-Al₂O₃ (1323c) catalyst. The spectrum of Ga-Al₂O₃ (1573c) resembles the calculated spectrum of α -Ga₂O₃. The experimental spectrum of α -Ga₂O₃ did not fit the calculated spectrum of α -Ga₂O₃ because it might contain an amorphous phase as a result of the low calcination temperature in preparation of α -Ga₂O₃.

Figures 7(c)-Exp. and **7(d)**-Calc. portray enlarged spectra of **Figs. 7(a)**-Exp. and **7(b)**-Calc. respectively. As shown in **Fig. 7(c)**-Exp., the transition energy of Ga-Al₂O₃ (1573c) is higher than that of the α -Ga₂O₃. The transition energy of Ga-Al₂O₃ (1323c) is higher than the that of the β -Ga₂O₃. As shown in **Fig. 7(d)**-Calc., the Al-substituted samples such as α -Ga₂O₃ (Al-rep) and β -Ga₂O₃ (Al-rep) have higher transition energies than those of α -Ga₂O₃ and β -Ga₂O₃ respectively. Therefore, the shift of the transition energy indicates the existence of Al near Ga because the coordination

Fig. 8 XANES Spectra by (a) Experiments and (b) Calculated for $\beta\text{-Ga}_2\text{O}_3$

environment of Ga in $\text{Ga-Al}_2\text{O}_3$ (1573c) and $\text{Ga-Al}_2\text{O}_3$ (1323c) includes the Al-Ga solid solution.

4. Discussion

$\text{Ga-Al}_2\text{O}_3$ (1323c) exhibited higher ethane conversion and the apparent activation energy of the catalytic reaction was 70 kJ mol^{-1} smaller than that on the gas phase reaction (bare Al_2O_3 without Ga). $\text{Ga-Al}_2\text{O}_3$ (1323c) exhibited lower ethylene selectivity than $\alpha\text{-Al}_2\text{O}_3$ (1573c) at the same conversion level. These results indicate that the $\text{Ga-Al}_2\text{O}_3$ (1323c) catalyst is applicable especially at low temperature.

Although the activity decreased with time on stream in case of $\text{Ga-Al}_2\text{O}_3$ (1573pc + 1323c), high catalytic activity was maintained over $\text{Ga-Al}_2\text{O}_3$ (1323c). As shown in Fig. 6, HAADF and EDX, the dispersion of Ga appears to be different depending on the support. Ga was highly dispersed on Al_2O_3 (1323c) and it led to high catalytic activity and stability. Unfortunately we could not determine the particle size of Ga from these data, so the discussion about turnover frequency (TOF) for Ga cannot be applicable in this case. As for the catalysts calcined at high temperature of 1573 K, although the Ga particle is also dispersed by HAADF, it showed rather low catalytic activity. The XANES spectra revealed that the crystalline structure of Ga was influenced by the calcination temperature. The structure of Ga, which is close to $\beta\text{-Ga}_2\text{O}_3$ in the $\text{Ga-Al}_2\text{O}_3$ (1323c) catalyst and is near $\alpha\text{-Ga}_2\text{O}_3$ when the catalyst calcined at 1573 K, affect the catalytic activity strongly. Some reports described that tetrahedral Ga shows high catalytic activity for dehydrogenation of propane^(18),21),22). The shape of the XANES spectra (Fig. 8) suggests that the proportion of tetrahedral Ga increased by forming Al-Ga solid solution. Therefore, this increase can be regarded as one reason for obtaining the high catalytic

performance. On the other hand, the structure of Ga on the catalyst calcined at 1573 K is close to $\alpha\text{-Ga}_2\text{O}_3$, similar to the $\alpha\text{-Al}_2\text{O}_3$ structure (the corundum structure). Accordingly, Ga in $\text{Ga-Al}_2\text{O}_3$ (1573c) is regarded as having 6 coordination and it leads to the low catalytic activity. On the $\text{Ga-Al}_2\text{O}_3$ (1323c) catalyst, it shows high activity because Ga is mainly existed in tetrahedral coordination state and it is highly dispersed, *i.e.* the high specific surface area of the active sites.

5. Conclusion

Screening results revealed that the Ga catalyst exhibited a high ethylene formation rate and better ethylene selectivity. For alumina-supported Ga catalysts, activity tests were conducted with changing the support and calcination temperature. The Ga catalyst supported on $\gamma\text{-Al}_2\text{O}_3$ and calcined at 1323 K showed a high ethylene formation rate and stability. However, catalysts calcined at 1573 K ($\text{Ga-Al}_2\text{O}_3$ (1573c) and $\text{Ga-Al}_2\text{O}_3$ (1573pc + 1573c)) showed low catalytic activities irrespective of the supports. The apparent activation energy was $283.7 \text{ kJ mol}^{-1}$ for the gas phase reaction, and $211.4 \text{ kJ mol}^{-1}$ for the surface reaction. Supporting $\text{Ga-Al}_2\text{O}_3$ (1323c) on the AFTALLOY can decrease the reaction temperature drastically thanks to its low apparent activation energy. Various analyses were conducted to elucidate the role of Ga. Results show that $\text{Ga-Al}_2\text{O}_3$ (1323c) had a high specific surface area and the supported Ga was finely dispersed. The Ga dispersion was maintained even after calcination at 1573 K or after reaction at 973 K. XANES spectra revealed that Ga on $\gamma\text{-Al}_2\text{O}_3$ calcined at 1323 K had a structure similar to $\beta\text{-Ga}_2\text{O}_3$ which included the large amount of the tetrahedral Ga species while the structure of Ga calcined at 1573 K came close to $\alpha\text{-Ga}_2\text{O}_3$ that had the octahedral Ga species. Based on the results presented above, Ga-

Al₂O₃ (1323c) exhibited high catalytic performance because highly dispersed tetrahedral Ga was supported by virtue of the high specific surface area of the γ -Al₂O₃ support and calcination at the optimum temperature.

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要 旨

エタン脱水素のための担持ガリウム酸化物触媒

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本研究では、エタンクラッカーの性能向上のために脱水素触媒を開発した。アルカンの脱水素触媒としてよく知られる Ga, Ge, In, Sn について検討した。これらの触媒について活性試験を行った結果、高い転化率とエチレン選択率を持つ Ga が最適であると考えた。Ga を α -Al₂O₃ に担持し 1323 K で焼成した触媒は経時的に活性が劣化する傾向を示したが、担体を γ -Al₂O₃

とした触媒は高いエチレン収率、安定性を示した。活性の差異について検討を深めるため、BET, XRD, EDX, XANES の分析を行った。この結果、Ga を γ -Al₂O₃ として担持した Ga 触媒は、担体が高比表面積かつ β -Ga₂O₃ に近い構造の Ga₂O₃ が高分散に担持されているため高い活性と安定性を示すということが考えられた。