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Dehydrogenation of propane over a silica-supported gallium oxide catalyst

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The dehydrogenation of propane over a silica-supported gallium oxide catalyst was investigated at temperatures ranging from 793 to 853 K under atmospheric pressure. The catalyst was found to be moderately active and highly selective to propene in the dehydrogenation of propane. The amount of carbonaceous deposits on the catalyst in the dehydrogenation was around 1/10th of that on a silica-supported chromium oxide catalyst. Lower reaction temperatures and lower concentrations of propane in the feed would be favorable for selective production of propene.

KEY WORDS: dehydrogenation; propane; propene; gallium oxide catalyst; silica; carbonaceous deposits.

1. Introduction

Propene is one of the most important commodity chemicals as a raw material of polymers or other chemical products. It is commercially produced by the separation of the products from FCC plants, or by the dehydrogenation of propane, or by the disproportionation of ethene/2-butene [1]. Chromium oxide-based catalysts have been used for the dehydrogenation of propane in the absence of hydrogen as a co-feed gas [1–3], whereas platinum-based catalysts have been used for the dehydrogenation of propane in the presence of hydrogen [1,4,5]. From environmental points of view, however, the catalysts not containing chromium are greatly desirable for the dehydrogenation of propane in the absence of hydrogen. Since it was reported that gallium oxide-based catalysts were moderately active for the dehydrogenation of propane [6–9], the authors have focused attention on gallium oxide–based catalysts for the dehydrogenation of propane.

In the present study, the dehydrogenation of propane over a silica-supported gallium catalyst was investigated. First, the catalytic performance of a silica-supported gallium catalyst for the dehydrogenation of propane was compared with that of a silica-supported chromium oxide catalyst, some of which was reported in our previous paper [10]. Then, the effects of reaction conditions on the catalytic performance of a silica-supported gallium oxide catalyst were investigated.

2. Experimental

A silica-supported gallium oxide or chromium oxide catalyst was prepared by an impregnation method using metal nitrates. CARiACT Q-6 supplied by Fuji Silysia Chemical Ltd. was used for a silica support. An aqueous solution of gallium nitrate or chromium nitrate was added to the silica. Then, the slurry was dried overnight at 383 K, and calcined at 873 K for 2 h. The content of gallium oxide or chromium oxide in the catalyst was 5 wt%. The molar content of gallium oxide or chromium oxide in the catalyst was 1.7 or 2.0 mol%. The surface areas of the two catalysts were 410 m^2/g.

The dehydrogenation of propane was carried out using a fixed bed flow reactor. The catalyst fixed in a reactor was treated with a co-feed gas (Ar or CO_2) before starting the reaction. Then, the dehydrogenation of propane was performed in the presence of Ar or CO_2 under atmospheric pressure at temperatures ranging from 793 to 853 K. The reaction products were analyzed by an FID gas chromatograph and by a TCD gas chromatograph directly connected to the reactor. The products in the dehydrogenation of propane in the absence of CO_2 were H_2, methane, ethane, ethene, propene, benzene, toluene, trace amounts of other aromatic hydrocarbons, C_4 and C_5 hydrocarbons. In the dehydrogenation in the presence of CO_2, CO was also formed in addition to the products in the dehydrogenation in the absence of CO_2. The yield of each product and the selectivity to each product were defined as the conversion of propane to the product and the yield of the product divided by the total conversion of propane, respectively.

The amount of carbonaceous deposits on the post-reaction catalyst was measured by TG/DTA. Tempera-

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ture programming reduction (TPR) measurements for the catalysts were carried out using a TCD in a stream of a gas mixture of H_2(10%) and Ar(90%) in the temperature range from 323 to 900 K. X-ray diffraction (XRD) measurements were also carried out to analyze the phases present in the catalyst. However, only a broad peak assigned to amorphous SiO_2 was detected for the catalyst samples used in the present study, suggesting that gallium oxide or chromium oxide could be highly dispersed on the silica.

3. Results and discussion

Figure 1 shows the yields of propene (Yield of C_3H_6) and of aromatics such as benzene, toluene and so on (Yield of Arom.), and the selectivities to propene (Sel. to C_3H_6) and to aromatics (Sel. to Arom.) in the dehydrogenation of propane in the presence of Ar or CO_2 over a silica-supported gallium oxide catalyst or over a silica-supported chromium oxide catalyst as a function of time on stream. The yields of propene and aromatics in the dehydrogenation over the gallium oxide catalyst in the presence of CO_2 were lower than those in the absence of CO_2. On the other hand, the yield of propene in the dehydrogenation over the chromium oxide catalyst in the presence of CO_2 was much higher than that in the absence of CO_2, as reported in our previous paper [10]. These findings suggest that the dehydrogenation over the gallium oxide catalyst would be inhibited by CO_2, whereas the dehydrogenation over the chromium oxide catalyst would be promoted by CO_2.

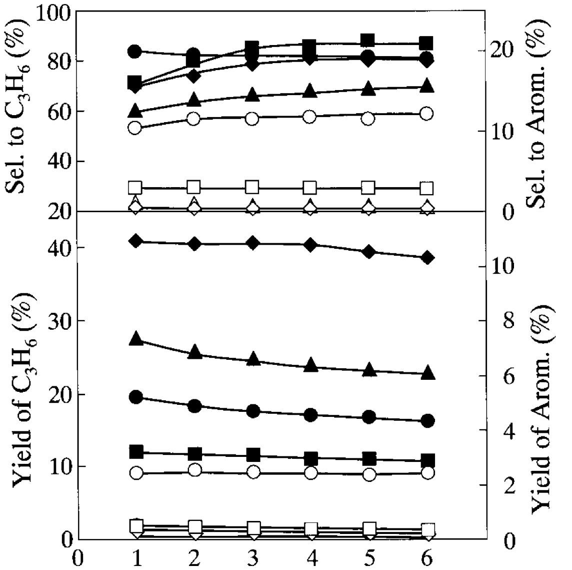

Figure 1. Yield of propene (●, ■, ▲, ◆) and aromatics (○, △, □, ◇), and the selectivities to propene (●, ■, ▲, ◆) and to aromatics (○, △, □, ◇) in the dehydrogenation of propane (C_3H_8) over a silica-supported gallium oxide catalyst (●, ■, ▲, ○, □) or over a silica-supported chromium oxide catalyst (▲, ◆, △, ◇) in the presence of Ar (●, ○, ▲, △) or CO_2 (■, □, ◆, ◇) as function of time on stream. Reaction conditions: 823 K; 0.1 MPa; C_3H_8 concentration in the feed (C_3H_8/Ar, C_3H_8/CO_2) = 10%, W/F = 22 g-cat/(mmol-C_3H_8/min).

TPR measurements for the catalysts, the results of which are shown in figure 2, indicate that the chromium oxide catalyst could be reduced at temperatures ranging from 573 to 873 K, as reported in our previous paper [10]. Our previous study also found that a part of the reduced chromium oxide catalyst could be reoxidized with CO_2 at 823 K [10]. On the other hand, figure 2 indicates that H_2O was not formed in the reduction of the gallium oxide catalyst with H_2. In addition, a TPR measurement for a Ga_2O_3 sample gave almost the same result as shown in figure 2. Although these findings may suggest that the gallium oxide catalyst would not be reduced with H_2 at temperatures less than 900 K, there might be some reduced $Ga^{+\delta}$ species in the gallium oxide catalyst during the dehydrogenation, as suggested in a previous paper [11]. More detailed investigation on the active sites and the reaction mechanisms for the dehydrogenation must be necessary for clearly explaining the difference between the catalytic performance of the gallium oxide catalyst and that of the chromium catalyst.

The yield of propene in the dehydrogenation of propane in the presence of Ar over the gallium oxide catalyst was 30% lower than that over the chromium oxide catalyst, as shown in figure 1. However, the selectivity to propene in the reaction over the gallium oxide catalyst (81%) was higher than that over the chromium catalyst (70%). And the selectivity to cracked products ($C_1 + C_2$ hydrocarbons) in the reaction over the gallium oxide catalyst (6%) was lower than that over the chromium catalyst (28%). The selectivity to aromatics in the dehydrogenation of propane in the presence of Ar over the gallium oxide catalyst (12%) was much higher than that over the chromium oxide catalyst (0.7%), suggesting that a much larger amount of

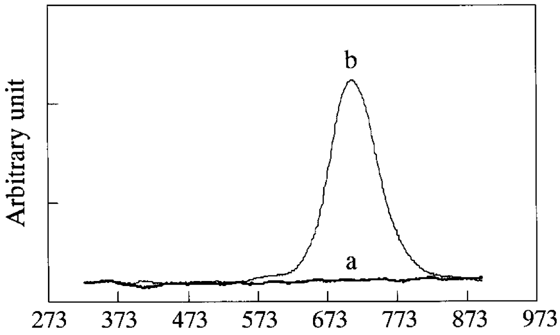

Figure 2. TPR profiles for a silica-supported gallium oxide catalyst (a) and for a silica-supported chromium oxide catalyst (b). The operating conditions for TPR measurement: 10 K/min; 0.1 Mpa; H_2/Ar = 1/9 (mol/mol); flow rate of H_2/Ar = 20 mL/ min.

acidic sites should be present in the gallium oxide catalyst. The acidic sites on both catalysts are now under investigation. The amount of carbonaceous deposits on the gallium oxide catalyst during the reaction was around 1/10th of that on the chromium oxide catalyst, as shown in table 1.

The findings described above suggest that the silica-supported gallium oxide catalyst should be suitable for the dehydrogenation of propane in the absence of CO_2. Therefore, further investigation was performed on the dehydrogenation over the gallium oxide catalyst in the presence of Ar.

Figure 3 shows the selectivities to propene, to aromatics and to cracked products as a function of propane conversion in the dehydrogenation of propane at 793 K. The dehydrogenation experiments were carried out at different W/Fs. The data shown in figure 3 were taken at 6 h after the beginning of the dehydrogenation. The selectivity to propene decreased with increasing C_3H_8 conversion, whereas the selectivity to aromatics increased and the selectivity to cracked products ($C_1 + C_2$) was almost unchanged with increasing C_3H_8 conversion. This finding strongly suggests that the reactions would proceed via the pathways shown in figure 4.

The dehydrogenation of propane over a catalyst bed of the gallium oxide catalyst (1 g) + the silica (1 g) was carried out at 823 K. The results obtained were almost the same as those in the reaction only over the gallium oxide catalyst (1 g). This finding suggests that the silica itself would be inactive for the dehydrogenation of propane as well as the aromatization and the cracking, and also that the aromatization of propene would occur on the gallium oxide catalyst. Accordingly, it is suggested that the gallium oxide would be active both for the formation of propene and for the aromatization of propene.

Figure 5 shows the effects of reaction temperature ranging from 793 to 853 K on the yields of propene and

Table 1
Amount of carbonaceous deposits on the catalyst during the dehydrogenation of propane over a silica-supported gallium oxide catalyst and over a silica-supported chromium oxide catalyst[a]

Catalyst[b]	Feed gas	Amount of carbonaceous deposits[c] (mg-C/g-cat)
Gallium oxide/SiO_2	C_3H_8/Ar	2
	C_3H_8/CO_2	2
Chromium oxide/SiO_2	C_3H_8/Ar	26
	C_3H_8/CO_2	19

[a] Reaction conditions: 823 K, atmospheric pressure, feed gas = $C_3H_8(10)/Ar(90)$ or $C_3H_8(10)/CO_2(90)$, W/F = 22 g-cat/(mmol-C_3H_8/min).

[b] The content of gallium oxide or chromium oxide in the catalyst was 5 wt%.

[c] 6 h after starting the reaction.

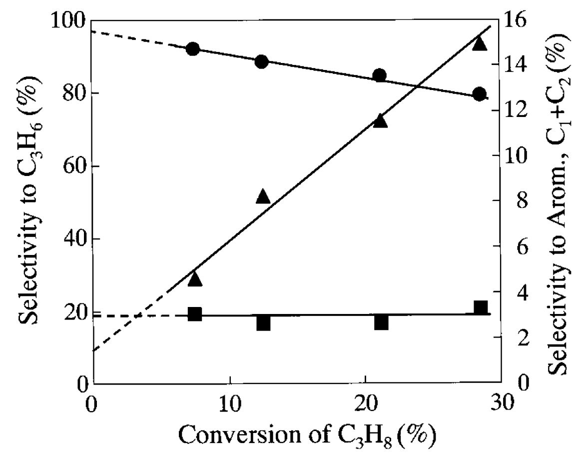

Figure 3. The selectivities to propene (●), to aromatics (▲) and to cracked products (■) as a function of the conversion of propane in the dehydrogenation over a silica-supported gallium oxide catalyst. Reaction conditions: 793 K; 0.1 MPa; C_3H_8 concentration in the feed (C_3H_8/Ar) = 10%.

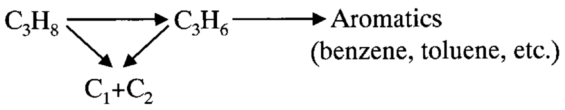

Figure 4. Reaction pathways in the dehydrogenation of propane over a silica-supported gallium oxide catalyst.

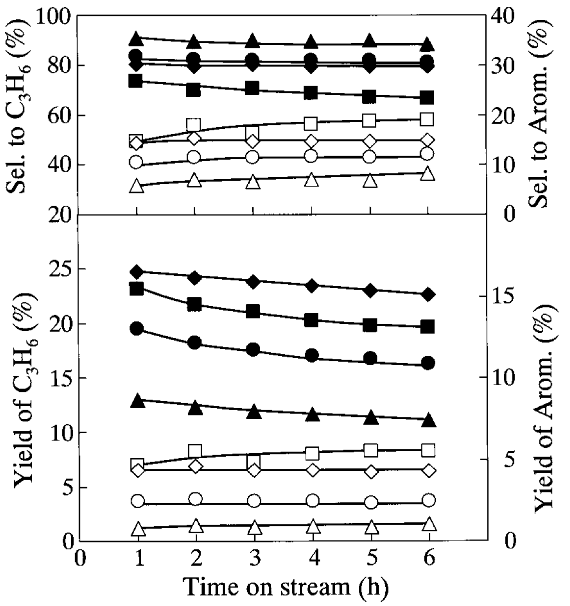

Figure 5. Effects of reaction temperature on the yields of propene (▲, ●, ■, ◆) and aromatics (△, ○, □, ◇) and the selectivities to propene (▲, ●, ■, ◆) and to aromatics (△, ○, □, ◇) in the dehydrogenation of propane over a silica-supported gallium oxide catalyst. Reaction conditions: 793 K (▲, △, ◆, ◇); 823 K (●, ○); 853 K (■, □); 0.1 MPa; C_3H_8 concentration in the feed (C_3H_8/Ar) = 10%; W/F = 22 (▲, ●, ■, △, ○, □) and 67 (◆, ◇) g-cat/(mmol-C_3H_8/min).

aromatics and on the selectivities to propene and to aromatics in the dehydrogenation of propane over the gallium oxide catalyst. The yields of propene, aromatics and cracked products at 6 h after the beginning of the reaction at a W/F of 22 g-cat/(mmol-C_3H_8/min) increased with increasing reaction temperature. The selectivity to propene at 6 h after the beginning of the reaction at a W/F of 22 g-cat/(mmol-C_3H_8/min) decreased from 88 to 67% with an increase in reaction temperature from 793 to 853 K, whereas the selectivity to aromatics and to cracked products increased from 8 to 19% and from 3 to 13% respectively. The amount of carbonaceous deposits on the catalyst during the dehydrogenation increased with increasing reaction temperature, as shown in table 2. Since the selectivity to each product could depend on the conversion of propane as shown in figure 3, the dehydrogenation of propane was carried out at 793 K and at a W/F of 67 g-cat/(mmol-C_3H_8/min) in order to obtain almost the same C_3H_8 conversion at 793 K and at 853 K (figure 5). The selectivity to propene at 793 K (79%) was higher than that at 853 K (67%), whereas the selectivities to aromatics and to cracked products at 793 K (15 and 3%) was lower than those at 853 K (19 and 13%). The findings described above suggest that lower reaction temperatures would be favorable for selective production of propene over the gallium oxide catalyst.

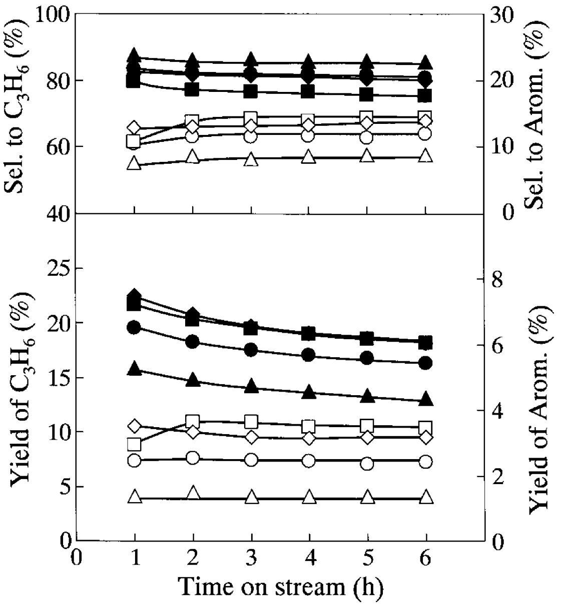

Figure 6. Effects of C_3H_8 concentration in the feed on the yields of propene (▲, ●, ■, ◆) and aromatics (△, ○, □, ◇) and the selectivities to propene (▲, ●, ■, ◆) and to aromatics (△, ○, □, ◇) in the dehydrogenation of propane over a silica-supported gallium oxide catalyst. Reaction conditions: 823 K; C_3H_8 concentration in the feed (C_3H_8/Ar) = 6% (▲, △, ◆, ◇); 10% (●, ○,); 17% (■, □); W/F = 22(▲, ●, ■, △, ○, □) and 33 (◆, ◇) g-cat/(mmol-C_3H_8/min).

Figure 6 shows the effects of propane concentration in the feed ranging from 6 to 17% on the yields of propene and aromatics and on the selectivities to propene and to aromatics in the dehydrogenation. The yields of propene, aromatics and cracked products at 6 h after the beginning of the reaction at a W/F of 22 g-cat/(mmol-C_3H_8/min) increased with an increase in the propane concentration in the feed from 6 to 17%. The selectivity to propene at 6 h after the beginning of the reaction at a W/F of 22 g-cat/(mmol-C_3H_8/min) decreased from 86 to 75% with an increase in the propane concentration from 6 to 17%, whereas the selectivity to aromatics and to cracked products increased from 9 to 14% and from 5 to 8% respectively. The amount of carbonaceous deposits on the catalyst during the dehydrogenation slightly increased with increasing propane concentration, as shown in table 2. In addition, the dehydrogenation of the feed containing 6% of propane was carried out at 823 K and at a W/F of 33 g-cat/(mmol-C_3H_8/min) in order to obtain almost the same conversion of C_3H_8 in the dehydrogenation of the feeds containing 6 and 17% of propane (figure 6). The selectivity to propene in the dehydrogenation of the feed containing 6% of propane (80%) was higher than that in the dehydrogenation of the feed containing 17% of propane (75%). The selectivity to aromatics in the dehydrogenation of the feed containing 6% of propane (14%) was almost the same as that in the dehydrogenation of the feed containing 17% of propane. The selectivity to cracked products in the dehydrogenation of the feed containing 6% of propane (5%) was lower than that in the dehydrogenation of the feed containing 17% of propane (8%). The findings described above suggest that lower concentrations of propane in the feed would be favorable for selective production of propene over the gallium oxide catalyst.

Table 2

Effects of reaction conditions of the amount of carbonaceous deposits on the catalyst during the dehydrogenation of propane over a silica-supported gallium oxide catalyst[a,b]

Temperature (K)	Concentration of propane in the feed gas mixture (%)	Amount of carbonaceous deposits[c] (mg-C/g-cat)
793		1
823	10.1	2
853		4
	5.9	1
823	10.1	2
	16.9	2

[a] Reaction conditions: 823 K, atmospheric pressure, W/F = 22 g-cat/(mmol-C_3H_8/min).

[b] The content of gallium oxide in the catalyst was 5 wt%.

[c] 6 h after starting the reaction.

In summary, the findings in the present study suggest that gallium oxide-based catalysts should be improved in their activities at lower temperatures and in their selectivity to propane for selective production of propene. The authors are now investigating the catalytic performances of gallium oxide-based catalysts supported on other materials and the active sites for the dehydrogenation of propane.

4. Conclusions

1. A silica-supported gallium oxide catalyst was found to be moderately active and highly selective to propene in the dehydrogenation of propane. The amount of carbonaceous deposits on the silica-supported gallium oxide catalyst in the dehydrogenation was around 1/10th of that on the silica-supported chromium oxide catalyst.
2. Lower reaction temperatures and lower concentrations of propane in the feed would be favorable for selective production of propene.

Acknowledgment

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