Effects of pre-treatment of a silica-supported gallium oxide catalyst with H_2 on its catalytic performance for dehydrogenation of propane

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The pre-treatment of a silica-supported gallium oxide catalyst with H_2 at 823 K increased the yield of aromatics and the selectivity to aromatics in the dehydrogenation of propane over the catalyst at 823 K. Gallium oxide in the catalyst was partially reduced with H_2 at 823 K. NH_3 desorption and DRIFTS studies on the gallium oxide catalyst suggest that the dehydrogenation of propane over a silica-supported gallium oxide catalyst would proceed in the following way: (1) the dehydrogenation of propane to produce propene would occur on Ga sites including $Ga^{\delta+}$–H sites and (2) the aromatization of propene to aromatics on Ga–O–H acid sites.

KEY WORDS: gallium oxide catalyst; silica; dehydrogenation; propane; aromatization; H_2 pre-treatment.

1. Introduction

From environmental points of view, the authors have focused attention on gallium oxide-based catalysts for developing high performance catalysts not containing chromium for the dehydrogenation of propane. The authors recently reported that a silica-supported gallium oxide catalyst was moderately active and highly selective to propene in the dehydrogenation of propane at temperatures ranging from 793 to 853 K and that the amount of carbonaceous deposits on the catalyst during the dehydrogenation was around one tenth of that on a silica-supported chromium oxide catalyst [1]. Furthermore, it was suggested that the aromatic products such as benzene, toluene and so on could be produced from propene on the acid sites on the gallium oxide contained in the catalyst.

In the present study, the effects of the pre-treatment of a silica-supported gallium oxide catalyst with H_2 on its catalytic performance for the dehydrogenation of propane were investigated. NH_3 desorption studies on the acid sites on the catalyst and DRIFTS studies on the gallium species on the catalyst surface were also performed. Furthermore, the reaction scheme of the dehydrogenation of propane over a silica-supported gallium oxide catalyst was discussed on the basis of the experimental findings.

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 mol% or 2.0 mol%. The surface areas of the two catalysts were 410 m^2/g. Gallium oxide supplied by Soekawa Chemicals Co., Ltd. was also used in the present work.

The dehydrogenation of propane was carried out using a fixed bed flow reactor. The catalyst fixed in a reactor was treated in a stream of H_2 or Ar at 823 K before starting the reaction. Then, the dehydrogenation of propane was performed in the presence of Ar under atmospheric pressure at 823 K. The reaction products were analyzed by a FID gas chromatograph and by a TCD gas chromatograph directly connected to the reactor. The products in the dehydrogenation of were H_2, methane, ethane, ethene, propene, benzene, toluene, trace amounts of other aromatic hydrocarbons, C_4 and C_5 hydrocarbons. 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 reduction of the catalyst in flowing H_2 at 823 K was carried using a flow reactor connected to a mass spectrometer (Microvision from Leda-Mass Ltd.). A small amount of the catalyst fixed in a sample tube was heated up to 823 K in a stream of He, and then He was switched to H_2. An effluent gas from the outlet of the sample tube was analyzed with the mass spectrometer. The signal of $m/e = 18$ which appear from H_2O was continuously monitored.

In order to characterize the acid sites on the catalyst surface, the desorption of NH_3 pulsed on the catalysts

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was carried out using a pulse reaction apparatus directly connected to the mass spectrometer. The catalyst fixed in a sample tube was treated with Ar or H_2 at 823 K. A small amount of NH_3 was introduced into the steam of Ar or H_2, while the temperature of the catalyst was kept at 823 K. An effluent gas from the outlet of the sample tube was analyzed with the mass spectrometer. The signals of $m/e = 16$, 17, 18 and 28 were simultaneously monitored. Since the signal of $m/e = 17$ might appear both from NH_3 and H_2O, the signal of $m/e = 16$ was taken as NH_3 in the effluent gas.

DRIFTS studies on the gallium species on the catalyst surface were performed using a FT-IR spectrometer (JIR-6500 from JEOL Ltd.) equipped with a MCT detector and a diffuse reflectance cell (Catalytic DRIFT Chamber from Spectra-Tech Inc.) to collect the diffuse reflectance spectra at 4 cm^{-1} resolution. The powder sample placed in the cell was treated in a stream of Ar or H_2 at 823 K. The diffuse reflectance spectra of the catalyst sample were taken at 743 K because the spectra taken at 823 K were not clear.

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 over a silica-supported gallium oxide catalyst pre-treated with H_2 or not pre-treated as a function of time on stream. The yield of aromatics and the selectivity to aromatics in the dehydrogenation over the gallium oxide catalyst not pre-treated with H_2 gradually increased with an increase in time on stream, suggesting that the number of the acid sites on the catalyst would increase during the dehydrogenation. The pre-treatment of the catalyst with H_2 increased the yield of aromatics and the selectivity to aromatics in the dehydrogenation of propane, whereas it reduced the yield of propene and the selectivity to propene and hardly altered the conversion of propane. This finding suggests that the aromatic products should be formed from propene, as suggested in our previous paper, and that the pre-treatment of the catalyst with H_2 could increase the number of the acid sites on the catalyst surface. This suggestion could also explain the increase of the aromatics yield in the dehydrogenation over the catalyst not pre-treated with increasing time on stream. On the other hand, the yield of aromatics in the dehydrogenation over the chromium oxide catalyst was very low, suggesting that the number of the acid sites on the chromium oxide catalyst should be very small.

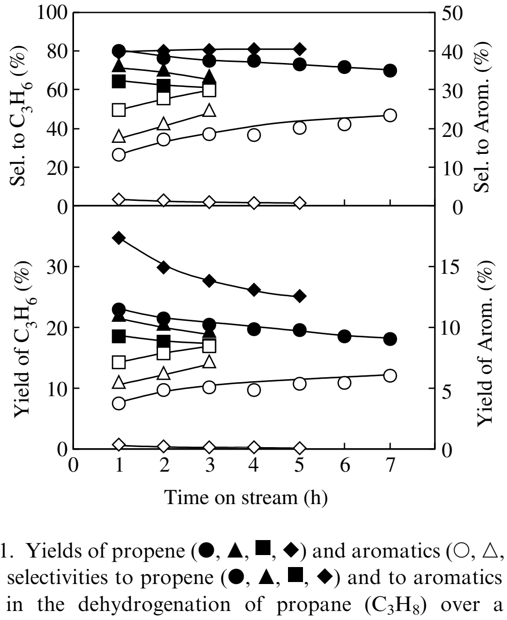

Figure 1. Yields of propene (●, ▲, ■, ◆) and aromatics (○, △, □, ◇), and the selectivities to propene (●, ▲, ■, ◆) and to aromatics (○, △, □, ◇) in the dehydrogenation of propane (C_3H_8) over a silica-supported gallium oxide catalyst not pre-treated (●, ○), a silica-supported gallium oxide catalyst pre-treated in H_2 for 0.5 h (▲, △), a silica-supported gallium oxide catalyst pre-treated in H_2 for 3 h (■, □) or a silica-supported chromium oxide catalyst pre-treated in H_2 for 3 h (◆, ◇) as a function of time on stream. Reaction conditions: 823 K; 0.1 MPa; C_3H_8 concentration in the feed (C_3H_8/Ar) = 10%, W/F = 22 g cat/(mmol C_3H_8/min).

In addition, the conversion of propane in the dehydrogenation over the gallium oxide catalyst hardly decreased during the first 7 h period, whereas the conversion of propane in the dehydrogenation over the chromium oxide catalyst greatly decreased during the first 5 h period, as shown in figure 1. The decrease in the activity of the chromium oxide catalyst should be due to a large amount of carbonaceous deposits on the catalyst, as suggested in our previous paper [1].

Unsupported Ga_2O_3 was also tested for the dehydrogenation of propane. The initial yield of propene (12%) in the dehydrogenation over the Ga_2O_3 pre-treated with H_2 at 823 K for 3 h was 45% lower than that (23%) in the dehydrogenation over the Ga_2O_3 not pre-treated, probably due to the decrease in the surface area of the Ga_2O_3 during the pre-treatment. However, the selectivity to aromatics (33%) in the dehydrogenation over the Ga_2O_3 pre-treated was 50% higher than that (21%) in the dehydrogenation over the Ga_2O_3 not pre-treated. This finding suggests that the acid sites for the aromatization of propene should be formed on the surface of Ga_2O_3 and that the pre-treatment of Ga_2O_3 with H_2 could increase the number of the acid sites on the Ga_2O_3.

The dehydrogenation of propane over a catalyst bed of the gallium oxide catalyst (1 g) + an alumina (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 Lewis acid sites of the alumina would be inactive for the dehydrogenation of propane as well as the aromatization and the cracking. In addition, the dehydrogenation of propane over a catalyst bed of the gallium oxide

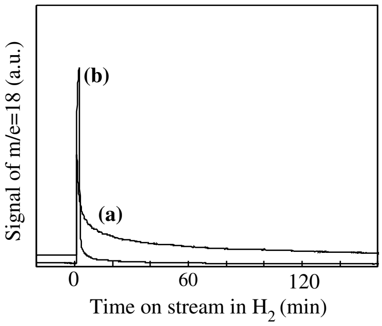

Figure 2. A signal of $m/e = 18$ as a function of time on stream in H_2 during the reduction of the gallium oxide catalyst: (a) or the chromium oxide catalyst; (b) at 823 K after raising the catalyst temperature up to 823 K in a stream of He. Operating conditions: the flow rate of H_2 (He) = 60 mL/min; the weight of sample = 0.2 g.

catalyst (1 g) + HY zeolite (0.5 g) was carried out at 823 K. Although the yield of the cracked products (C_1 + C_2 hydrocarbons) was very high, the ratio of the aromatics yield to the propene yield was more than twice higher than that in the dehydrogenation only over the gallium oxide catalyst, suggesting that Brønsted acid sites of HY could catalyze the cracking and the aromatization. The findings described above suggest that the aromatization of propene could take place on Brønsted acid sites, not on Lewis acid sites. Accordingly, it is also suggested that the pre-treatment of the silica-supported gallium oxide catalyst with H_2 could increase the number of Brønsted acid sites.

Figure 2 shows a signal of $m/e = 18$ during the reduction of the catalyst with H_2 at 823 K as a function of time on stream in H_2. The present finding suggests that a part of the gallium oxide on the silica could be reduced in a stream of H_2 and that the gallium oxide on the silica should be more difficult to be reduced than the chromium oxide on the silica. The same reduction experiment for CuO/ZnO was carried out at 403 K, the CuO of which was completely reduced. The comparison of the $m/e = 18$ peak area in the reduction of CuO/ZnO with that in the reduction of the gallium oxide catalyst indicated that about 30% of O in the Ga_2O_3 contained in the catalyst was removed as H_2O during the reduction in H_2 at 823 K. This finding suggests that Ga_2O_3 particles in the catalyst could be partially reduced in H_2 at 823 K.

Desorption measurements of NH_3 pulsed on the catalyst were carried out at 823 K in order to clarify the effect of pre-treatment of the catalyst with H_2 on the number of the acid sites on the catalyst at the temperature in the dehydrogenation. The results of the measurements are shown in figure 3. The retention time of NH_3 on the gallium oxide catalyst increased with an increase in the pre-treatment period. This finding strongly supports the suggestion previously described that the pre-treatment of the gallium oxide catalyst with H_2 could increase the number of acid sites on the catalyst. On the other hand, the retention time of NH_3 on the chromium oxide catalyst was much shorter than that on the gallium oxide catalyst, suggesting that number of the acid sites on the chromium oxide catalyst should be very small.

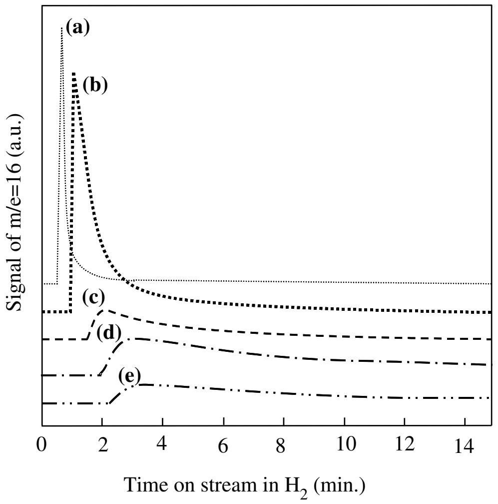

Figure 3. A signal of $m/e = 16$ in the effluent gas after a small amount of NH_3 was pulsed at 823 K over the silica pre-treated in H_2 at 823 K for 1 h (a), the chromium oxide catalyst pre-treated in H_2 at 823 K for 3 h (b), the gallium oxide catalyst pre-treated in Ar at 823 K for 1 h (c), the gallium oxide catalyst pre-treated in H_2 at 823 K for 0.5 h (d) or the gallium oxide catalyst pre-reduced in H_2 at 823 K for 3 h (e) as a function of time on stream in H_2 (a, b, d, e) or Ar (c). Operating conditions: 0.1 MPa; temperature of the sample = 823 K; flow rate of H_2 or Ar = 20 mL/min; NH_3/Ar = 1/9 (mol/mol).

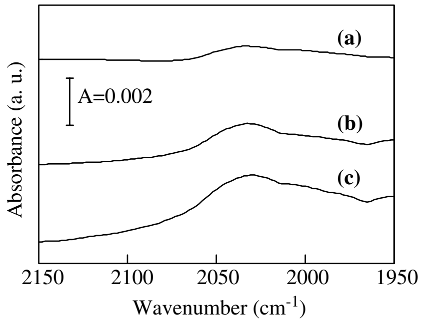

Figure 4. FTIR spectrum at 743 K of the gallium oxide catalyst pre-treated in H_2 at 743 K for 0.5 h (a), for 1.5 h (b) or for 3 h (c).

Figure 4 shows DRIFTS profiles for the catalyst pre-treated in flowing H_2 at 743 K, indicating that the band at 2020 cm^{-1} increased with an increase in the pre-treatment period. Since the band at 2020 cm^{-1} was previously assigned as $Ga^{\delta+}$–H bond [2,3], figure 4 suggests that the pre-treatment of the catalyst with H_2 could increase the number of $Ga^{\delta+}$–H bonds on the catalyst. The previous studies suggest that $Ga^{\delta+}$–H bonds on the gallium oxide catalyst should be formed by heterolytic dissociation of H_2 molecule to yield additional Ga–O–H bonds [2–4]. Although the band around at 3640 cm^{-1} which is assigned as O–H bond was not clearly detected owing to the overlapping with the O–H bond of Si–OH groups, Ga–O–H bonds might be the acid sites for the aromatization of propene. In addition, the finding that the pre-treatment of the catalyst with H_2 hardly altered the conversion of propane in the dehydrogenation, as described earlier, suggests that the dehydrogenation of propane to propene should occur on Ga sites including Ga–H sites.

In summary, the findings in the present work suggest that the dehydrogenation of propane over a silica-supported gallium oxide catalyst would proceed in the following way: (1) the dehydrogenation of propane to produce propene would occur on Ga sites including Ga–H sites and (2) the aromatization of propene to aromatics on Ga–O–H acid sites.

4. Conclusions

1. The pre-treatment of a silica-supported gallium oxide catalyst with H_2 at 823 K increased the yield of aromatics and the selectivity to aromatics in the dehydrogenation of propane over the catalyst at 823 K.
2. The gallium oxide in the catalyst could be partially reduced with H_2 at 823 K.
3. NH_3 desorption studies on the gallium oxide catalyst suggest that the pre-treatment of the catalyst with H_2 at 823 K could increase the number of acid sites on the catalyst.
4. DRIFTS studies on the gallium species on the catalysts surface suggest that the pre-treatment of the catalyst with H_2 at 823 K could increase the number of $Ga^{\delta+}$–H bonds on the surface of the catalyst.
5. The findings in the present work suggest that the dehydrogenation of propane over a silica-supported gallium oxide catalyst would proceed in the following way: (1) the dehydrogenation of propane to produce propene would occur on Ga sites including $Ga^{\delta+}$–H sites and (2) the aromatization of propene to aromatics on Ga–O–H acid sites.

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