Dehydrogenation of ethane on Ga oxide catalysts

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Abstract: Catalysts for dehydrogenation of ethane were investigated for lowering cracking temperatures of ethane. Although Ga/α-Al_2O_3 catalyst showed high activity for dehydrogenation of ethane, it showed low stability. On the other hand, Ga/γ-Al_2O_3 calcined at 1323 K showed high activity and stability. To elucidate the effects of support and calcination temperature on the catalytic performance, XRD, TEM-EDX and XANES measurements were conducted. XRD revealed that only Ga/γ-Al_2O_3 calcined at 1323 K contained θ-Al_2O_3. TEM and XANES revealed that Ga was highly dispersed and the tetrahedral Ga mainly existed on the catalyst. Therefore, highly dispersed tetrahedral Ga would contribute to the high activity and stability.
Keywords: Dehydrogenation of ethane, Ga catalyst, Calcination temperature.

1. Introduction

Ethylene is one of the important chemicals for plastics. In the petroleum industry, ethylene is produced by steam cracking of naphtha. Recently, raw materials for ethylene production have shifted from naphtha to ethane because ethane is a cheap feedstock due to the shale revolution[1)]. However, in the process of ethane cracking, coke formation is a serious problem because it reduces the productivity[2)]. To solve the problem, coating a catalyst on the cracking coil for dehydrogenation of ethane is expected to suppress coke formation by lowering the reaction temperature. Therefore, we investigated metal oxide catalysts supported on α-Al_2O_3 as a model of the surface of the cracking coil. Ga/α-Al_2O_3 showed high catalytic performance. In addition, Ga/γ-Al_2O_3 or α-Al_2O_3 calcined at 1323 K or 1573 K were prepared to improve the dispersion of Ga and to form the solid solution. Various characterizations were also conducted to elucidate the nature of Ga species.

2. Experimental (or Theoretical)

The γ-Al_2O_3 (JRC-ALO-6) support was crashed into powder by a planetary ball mill (P-6; Fritsch GmbH). The α-Al_2O_3 support was prepared by calcining γ-Al_2O_3 in air at 1573 K for 3 h. Ga, Ge, In or Sn catalyst supported on α-Al_2O_3 was prepared by an impregnation method. The calcination temperature after metal loading was 1323 K. In addition, Ga/α-Al_2O_3 and Ga/γ-Al_2O_3 calcined at 1323 or 1573 K were prepared by the impregnation method. Ga catalysts are denoted as Ga-Al_2O_3 (1573pc+*x*c). The pre-calcination (pc) temperature before Ga loading is shown in case of α-Al_2O_3. Pre-calcination temperature is not shown when γ-Al_2O_3 was used. The calcination (c) temperature after Ga loading is denoted as *x*.

Catalytic activity tests were conducted in a fixed bed flow reactor at atmospheric pressure. The catalyst was sieved into 420-840 μm and 100 mg of the catalyst was charged into the quartz tube (4 mm i.d.) with SiC (392 mg). The furnace was heated to 973 K. The feed gas composition was C_2H_6 : H_2O : N_2 = 1 : 1.36 : 5.41 at a total flow rate of 281.6 SCCM. Products were analyzed using a GC-FID with a methanizer (Ru/Al_2O_3).

Characterizations including XRD, TEM-EDX and XANES measurements were conducted. Plane wave basis pseudopotential calculations were implemented in the CASTEP code[3)] to simulate XANES spectra. Details are written in the literature[4)].

3. Results and discussion

As reported previously, Ga-Al_2O_3 (1573pc+1323c) showed a high catalytic performance[4]. However, it showed low catalytic stability. Then, to improve the dispersion of Ga, catalysts were prepared using γ-Al_2O_3 as a support, which has higher specific surface area than α-Al_2O_3. In addition, the Ga catalysts supported on α-Al_2O_3 or γ-Al_2O_3 were calcined at 1573 K to form the solid solution. Figure 1 shows C_2H_4 formation rate with time on stream on each catalyst. From the results, Ga-Al_2O_3 (1323c) showed a high catalytic activity and stability.

Various characterizations were conducted to elucidate why Ga-Al_2O_3 (1323c) exhibited high catalytic performance. X-ray diffraction (XRD) analysis revealed that only Ga-Al_2O_3 (1323c) contained θ-Al_2O_3 structure and the others calcined at 1573 K contained α-Al_2O_3 structure. Peaks attributed to Ga species were not observed because Ga species were highly dispersed. Next, HAADF images and EDX mappings by FE-TEM were measured to evaluate the dispersion of Ga on the catalysts. As a result, Ga was highly dispersed on Ga-Al_2O_3 (1323c) whereas Ga was agglomerated on Ga-Al_2O_3 (1573pc+1323c). Ga *K*-edge XANES spectra were measured to investigate the coordination environment and the electronic state of Ga species on the catalysts. In addition, XANES spectra for α-Ga_2O_3, β-Ga_2O_3, α-Ga_2O_3 "Al-rep" and β-Ga_2O_3 "Al-rep" were calculated. The description "Al-rep" shows the replacement of some Ga ions with Al ions. XANES spectra revealed that Ga-Al_2O_3 (1323c) had a similar structure to β-Ga_2O_3. Comparing the experimental spectra with calculated ones, the formation of Al_2O_3-Ga_2O_3 solid solution was confirmed in Ga-Al_2O_3 (1323c). In addition, Ga-Al_2O_3 (1323c) contains a large amount of tetrahedral Ga. Chen *et al*. reported that the tetrahedral Ga shows high activity for dehydrogenation of propane[5]. The highly dispersed tetrahedral Ga species on Ga-Al_2O_3 (1323c) with highly dispersed contributes to the high activity and stability for dehydrogenation of ethane.

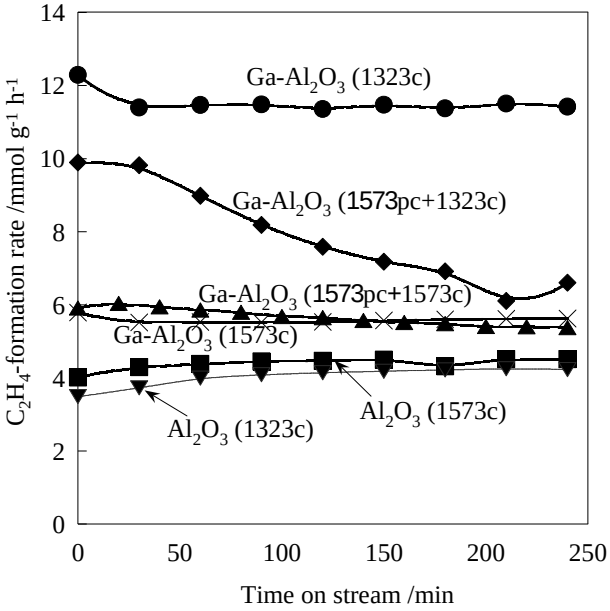

Figure 1. Activity test for various Ga-catalysts at 973 K[4].

4. Conclusions

We investigated catalysts for dehydrogenation of ethane to lower reaction temperature of ethylene formation. Ga-Al_2O_3 (1323c) showed high catalytic activity and stability. XRD analysis revealed only Ga-Al_2O_3 (1323c) contained θ-Al_2O_3 structure while the other catalysts contained α-Al_2O_3 structure. From the results of TEM-EDX, Ga was highly dispersed on Ga-Al_2O_3 (1323c) than Ga-Al_2O_3 (1573pc+1323c). The experimental and theoretical XANES spectra revealed that Al_2O_3-Ga_2O_3 solid solution with tetrahedral Ga species existed on Ga-Al_2O_3 (1323c). Therefore, Ga-Al_2O_3 (1323c) showed high catalytic performance thanks to the presence of highly dispersed and tetrahedral coordination Ga species.

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