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Dehydrogenation of propane over a silica-supported vanadium oxide catalyst

Isao Takahara*, Masahiro Saito, Megumu Inaba, and Kazuhisa Murata

Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba-shi, Ibaraki-ken, 305-8569, Japan

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The dehydrogenation of propane over a silica-supported vanadium oxide catalyst was investigated at 823 K under atmospheric pressure in the presence/absence of CO_2. The yield of propene and the selectivity to propene were higher in the dehydrogenation in the presence of CO_2 than those in the dehydrogenation in the absence of CO_2. On the other hand, the yield of aromatics and the selectivity to aromatics were much higher in the dehydrogenation in the absence of CO_2 than those in the dehydrogenation in the presence of CO_2. TPR measurements, NH_3 desorption studies and *in-situ* UV–vis studies on the catalyst were also performed to elucidate the effects of CO_2 on the behavior of the vanadium oxide in the catalyst during the dehydrogenation of propane.

KEY WORDS: dehydrogenation; propane; propene; vanadium oxide catalyst; silica.

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 K to 853 K [1,2].

In the present study, the dehydrogenation of propane over a silica-supported vanadium oxide catalyst was investigated. First, the catalytic performance of a silica-supported vanadium oxide catalyst for the dehydrogenation of propane at 823 K was examined in the presence/absence of CO_2. Then, the reduction of the vanadium oxide catalyst in a stream of H_2 was investigated. NH_3 desorption studies on the acid sites on the catalyst and *in-situ* UV–vis studies on the vanadium species on the catalyst were also performed. Furthermore, the effects of CO_2 on the behavior of the vanadium oxide in the catalyst during the dehydrogenation of propane were discussed on the basis of the experimental findings.

2. Experimental

A silica-supported vanadium oxide was prepared by an impregnation method using ammonium vanadate (V). CARiACT Q-6 supplied by Fuji Silysia Chemical Ltd. was used for a silica support. An aqueous solution of ammonium vanadate was added to the silica. Then, the slurry was dried overnight at 383 K, and calcined at 923 K for 2 h. The content of vanadium oxide in the catalyst was 5 wt%. The molar content of vanadium oxide in the catalyst was 1.7 mol%. The surface area of the catalyst was 350 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 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 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.

Temperature programming reduction (TPR) measurements for the catalyst were carried out using a thermal conductivity detector in a stream of a gas mixture of H_2 (10%) and Ar (90%) in the temperature range from 323 to 923 K under the following operation conditions: 0.1 MPa, flow rate of H_2/Ar = 20 mL/min, heating rate = 1 K/min. The reduction of the catalyst in

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* To whom correspondence should be addressed.
E-mail: i.takahara@aist.go.jp

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flowing H_2 at 823 K was also carried using a flow reactor connected to a mass spectrometer (Microvision from Leda-Mass Ltd.). The details of the reduction procedure are described elsewhere [2].

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 vanadium oxide could be highly dispersed on the silica.

In order to characterize the acid sites on the catalyst surface, the desorption of NH_3 pulsed on the catalyst at 823 K was carried out using a pulse reaction apparatus directly connected to the mass spectrometer. The details of the NH_3 desorption procedure are described elsewhere [2].

In-situ UV–vis spectroscopic studies on the vanadium species in the catalyst were performed using a UV/VIS/NIR spectrometer (V-570 from JASCO Corp.) equipped with a spectrophotometer and a diffuse reflectance cell supplied from JASCO Corp. The powder sample placed in the cell was treated in a stream of Ar, H_2 or CO_2 at 823 K, and the spectra were taken in the range of 200–800 nm with a reference of $BaSO_4$ at 603 K, because the spectra taken at higher temperatures were not clear.

3. Results and discussion

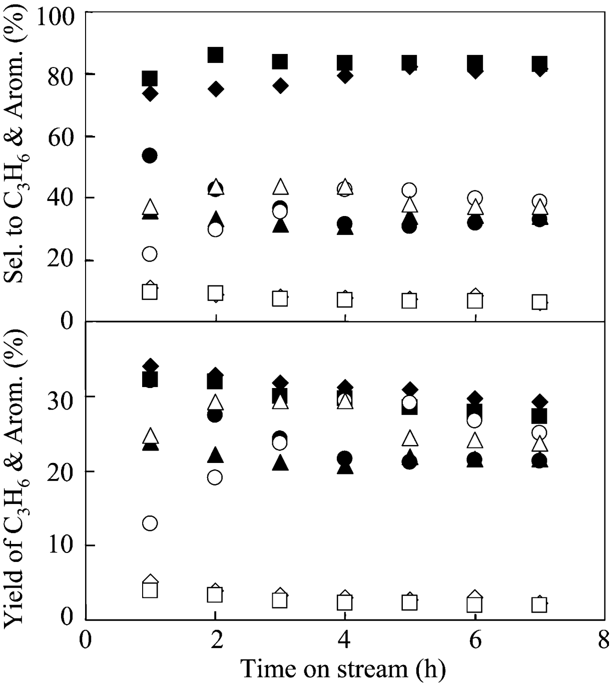

Figure 1. Yields of propene (●, ▲, ■, ◆) and aromatics (○, △, □, ◇), and the selectivities to propene (●, ▲, ■, ◆) and to aromatics (○, △, □, ◇) in the dehydrogenation of propane (C_3H_8) over a silica-supported vanadium oxide catalyst not pre-treated (●, ○, ◆, ◇) or over a silica-supported vanadium oxide catalyst pre-treated in H_2 for 2 h (▲, △, ■, □) in the presence of Ar (●, ○, ▲, △) or in the presence of CO_2 (■, □, ◆, ◇) 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 = 45 g-cat/(mmol-C_3H_8/min).

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 vanadium oxide catalyst as a function of time on stream. The yield of propene and the selectivity to propene in the dehydrogenation over the vanadium oxide catalyst in the presence of CO_2 were higher than those in the absence of CO_2. On the other hand, the yield of aromatics and the selectivity to aromatics in the dehydrogenation over the vanadium oxide catalyst in the presence of CO_2 was much lower than those in the absence of CO_2. And the conversion of propane in the dehydrogenation in the presence of CO_2 was a little lower than that in the absence of CO_2. These findings suggest that the dehydrogenation over the vanadium oxide catalyst would be slightly inhibited by CO_2 and that CO_2 would suppress the aromatization of propene to lead to a higher yield of propene and a higher selectivity to propene in the dehydrogenation in the presence of CO_2 than in the dehydrogenation in the absence of CO_2. In the case of the dehydrogenation in the absence of CO_2, the pre-treatment of the catalyst with H_2 increased the yield of aromatics and the selectivity to aromatics in the dehydrogenation of propane at 1–3 h of time on stream, whereas it reduced the yield of propene and the selectivity to propene and hardly altered the conversion of propane. In the case of the dehydrogenation in the presence of CO_2, the pre-treatment of the catalyst with H_2 hardly altered the yields of aromatics and propene and the selectivities to aromatics and to propene in the dehydrogenation. These findings suggest 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 in the yield of aromatics with increasing time on stream during the dehydrogenation in the absence of CO_2 over the catalyst not pre-treated in H_2. Furthermore, it is also suggested that CO_2 could reduce the number of acid sites on the catalyst surface.

In addition, the dehydrogenation of propane over bulk V_2O_5 in the presence/absence of CO_2 was also carried out. The initial yield of aromatics in the dehydrogenation in the absence of CO_2 was three times higher than that in the dehydrogenation in the presence of CO_2. The activity of bulk V_2O_5 rapidly decreased with time on stream in the dehydrogenation in the absence of CO_2, whereas it slowly decreased with time on stream in the dehydrogenation in the presence of CO_2. These findings suggest that the catalytic properties of vanadium oxide in the silica-supported vanadium oxide catalyst should be almost the same as that of bulk

V_2O_5, and that the acid sites should be formed on vanadium oxide in the catalyst.

The amount of carbonaceous deposits on the catalyst during the dehydrogenation in the presence of CO_2 was much smaller than that during the dehydrogenation in the absence of CO_2, as shown in figure 2. This finding might be related to the finding described above that the yield of aromatics and the selectivity to aromatics in the dehydrogenation in the presence of CO_2 was much lower than those in the absence of CO_2. Furthermore, all findings described above suggest that the state of the vanadium oxide in the catalyst in the dehydrogenation in the presence of CO_2 should be much different from that in the dehydrogenation in the absence of CO_2. Accordingly, the characterization of the vanadium oxide in the catalyst in the presence/absence of CO_2 must be necessary.

TPR measurements for the fresh catalyst and for the catalyst treated with CO_2 after the first TPR measurement, the results of which are shown in figure 3, suggest that vanadium oxide in the catalyst could be reduced at temperatures ranging from 723 to 873 K and that a part of the reduced vanadium oxide in the catalyst could be re-oxidized with CO_2 at 823 K. The peak area for the catalyst treated with CO_2 after the first TPR measurement was about 30% of that for the fresh catalyst. The results of the reduction experiments in a stream of H_2 at 823 K for the fresh catalyst and for the catalyst treated with CO_2 at 823 K after the first reduction are shown in Figure 4. In addition, the oxidation of reduced vanadium oxide in the catalyst with CO_2 was carried out. When a small amount of CO_2 was pulsed at 823 K to the catalyst reduced at 823 K with H_2, some amount of CO was detected in an effluent gas. These findings strongly supports the suggestion described above.

Desorption measurements of NH_3 pulsed to the catalyst were carried out at 823 K in order to clarify the effects of pre-treatment of the catalyst with H_2 and of re-treatment of the catalyst with CO_2 after the first reduction on the number of the acid sites on the catalyst at the temperature of the dehydrogenation. The results of the measurements are shown in figure 5. The pre-treatment of the catalyst with H_2 at 823 K increased the retention time of NH_3 on the vanadium oxide catalyst. This finding strongly supports the suggestion previously described that the pre-treatment of the vanadium 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 catalyst re-treated with CO_2 after the first reduction was almost the same as that on the catalyst treated in Ar, suggesting that CO_2 could reduce the

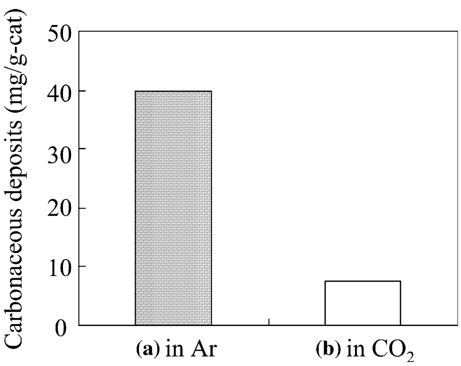

Figure 2. Amount of carbonaceous deposits on a silica-supported vanadium oxide catalyst during the dehydrogenation of propane for 7 h in the presence of Ar (a) or in the presence of CO_2 (b). Reaction conditions were the same as shown in figure 1.

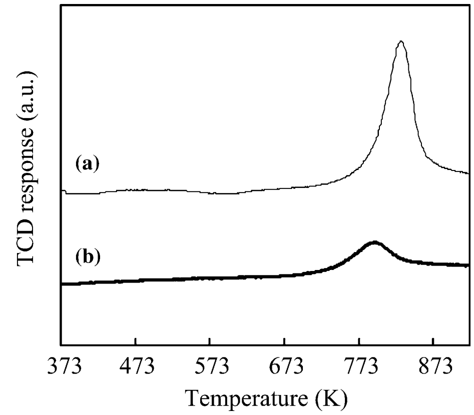

Figure 3. TPR profiles of a fresh silica-supported vanadium oxide catalyst (a) and of a silica-supported vanadium oxide catalyst treated with CO_2 at 823 K for 1 h after the first reduction (b) in a stream of a gas mixture of H_2 (10%) and Ar (90%) in the temperature range from 323 to 923 K. Operation conditions: 0.1 MPa; $H_2/Ar = 1/9$; flow rate of $H_2/Ar = 20$ mL/min; heating rate = 10 K/min.

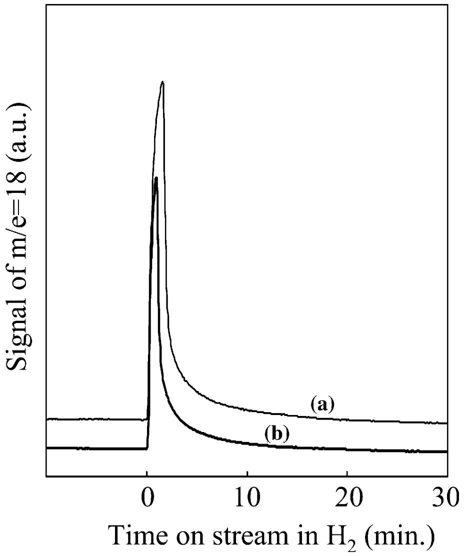

Figure 4. A signal of m/e = 18 as a function of time on stream in H_2 during the reduction of a fresh silica-supported vanadium oxide catalyst (a) or of a silica-supported vanadium oxide catalyst treated with CO_2 at 823 K for 1 h after the first reduction (b) at 823 K after raising the catalyst temperature up to 823 K in a stream of He. Operating conditions: 0.1 MPa,; the flow rate of H_2 (He) = 60 ml/min; the weight of sample = 0.2 g.

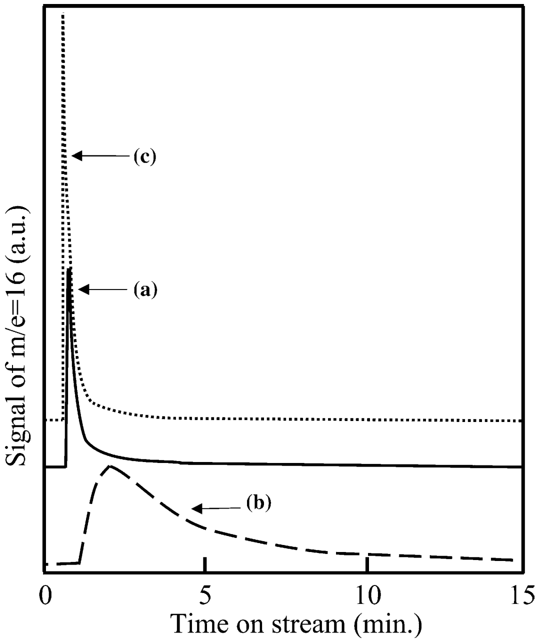

Figure 5. A signal of m/e = 16 in the effluent gas after a small amount of NH_3 was pulsed at 823 K over the vanadium oxide catalyst pre-treated in Ar at 823 K for 1 h (a), the vanadium oxide catalyst pre-treated in H_2 at 823 K for 2 h (b) or the vanadium oxide catalyst treated with CO_2 at 823 K for 1 h after the first pre-treatment in H_2 at 823 K for 2 h (c) as a function of time on stream in Ar (a, c) or in H_2 (b). Operating conditions: 0.1 MPa; temperature of the sample = 823 K; flow rate of Ar or H_2 = 20 ml/min; NH_3/Ar = 1/9 (mol/mol).

number of the acid sites on the catalyst, as previously described.

Figure 6 shows *in situ* UV–vis spectra of the catalyst treated at 823 K under various gas compositions. In the case of the catalyst treated at 823 K in Ar, UV–vis absorption bands located below 400 nm, which should be assigned to the oxygen ligand to metal charge transfer bands of V^{5+} [3,4], were observed. On the other hand, in the case of the catalyst treated at 823 K in H_2/Ar, a UV–vis absorption bands above 400 nm, which should be assigned to a week d-d transition of V^{4+}/V^{3+} [3], were observed and UV–vis absorption bands below 400 nm decreased. In the case of the catalyst treated at 823 K with CO_2 after the first reduction, UV–vis absorption bands below 400 nm increased and UV–vis absorption bands above 400 nm decreased. These findings suggest that the vanadium on the surface of vanadium oxide in the catalyst could be V^{4+}/V^{3+} in H_2 and in the dehydrogenation in the absence of CO_2, whereas that could be V^{5+} in the dehydrogenation in the presence of CO_2 by the oxidizing action of CO_2.

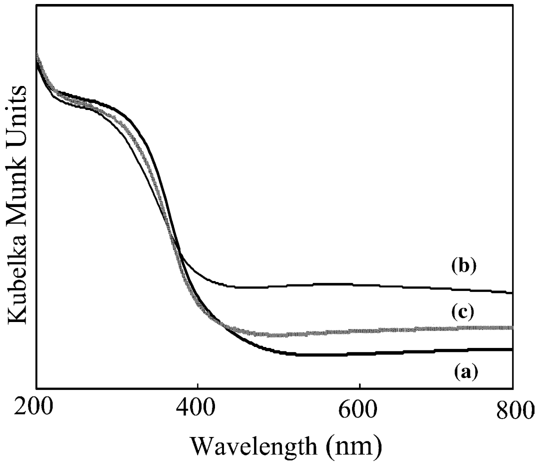

Figure 6. *In-situ* UV–vis diffuse reflectance spectrum at 603 K of the vanadium oxide catalyst pre-treated in Ar at 823 K for 1 h (a), the vanadium oxide catalyst pre-treated in H_2/Ar at 823 K for 2 h (b) or the vanadium oxide catalyst treated with CO_2 at 823 K for 1 h after the first pre-treatment in H_2 at 823 K for 2 h (c). Operation conditions: 0.1 MPa; 603 K; flow rate of Ar, H_2/Ar or CO_2 = 60 ml/min; H_2/Ar = 1/9 (mol/mol).

Although DRIFTS measurements on the catalyst were made in order to obtain some useful information about acid sites on reduced vanadium oxide in the catalyst, the band which should be assigned to O–H bond of V–O–H could not be clearly detected owing mainly to the overlapping with O–H bond of Si–OH groups. However, the experimental findings in the present study are very similar to those in our previous study on the dehydrogenation of propane over a silica-supported gallium oxide catalyst. Accordingly, it is suggested that the acid sites on vanadium oxide would be V–O–H sites adjacent to V^{4+}/V^{3+} sites like Ga–O–H sites adjacent to Ga^{δ} sites which was suggested in our previous study [2].

In summary, the findings in the present study suggest that the vanadium in the silica-supported vanadium oxide catalyst could be reduced to V^{4+}/V^{3+} in the dehydrogenation of propane in the absence of CO_2 to lead to the formation of acid sites on the surface of the vanadium oxide. The acid sites formed could produce a higher yield of aromatics and a larger amount of carbonaceous deposits. The present findings also suggest that the vanadium on the surface of vanadium oxide in the dehydrogenation of propane in the presence of CO_2 could be V^{5+} which could not lead to the formation of acid sites but result in a higher yield of propene and a smaller amount of carbonaceous deposits.

4. Conclusions

1. The dehydrogenation of propane over a silica-supported vanadium oxide catalyst was investigated at 823 K in the presence/absence of CO_2. The yield of propene and the selectivity to propene were higher in the dehydrogenation in the presence of CO_2 than those in the dehydrogenation in the absence of CO_2. On the other hand, the yield of aromatics and the selectivity to aromatics were much higher in the dehydrogenation in the absence of CO_2 than those in the dehydrogenation in the presence of CO_2. In

addition, the amount of carbonaceous deposits on the catalyst during the dehydrogenation in the presence of CO_2 was smaller than that during the dehydrogenation in the absence of CO_2.

2. The vanadium oxide in the catalyst could be reduced at temperatures ranging from 723 to 873 K and a part of the reduced vanadium oxide in the catalyst could be re-oxidized with CO_2 at 823 K.
3. NH_3 desorption studies on the vanadium oxide catalyst suggest that the pre-treatment of the vanadium oxide catalyst with H_2 could increase the number of acid sites on the catalyst and that CO_2 could reduce the number of the acid sites on the catalyst.
4. UV–vis studies on the vanadium oxide in the catalyst suggest that the vanadium on the surface of vanadium oxide in the catalyst could be V^{4+}/V^{3+} in H_2 and in the dehydrogenation in the absence of CO_2, whereas that could be V^{5+} in the dehydrogenation in the presence of CO_2 by the oxidizing action of CO_2.
5. The findings in the present study suggest that the vanadium in the silica-supported vanadium oxide catalyst could be reduced to V^{4+}/V^{3+} in the dehydrogenation of propane in the absence of CO_2 to lead to the formation of acid sites on the surface of the vanadium oxide. The acid sites formed could produce a higher yield of aromatics and a larger amount of carbonaceous deposits. It is also suggested that the vanadium on the surface of vanadium oxide in the dehydrogenation of propane in the presence of CO_2 could be V^{5+} which could not lead to the formation of acid sites but result in a higher yield of propene and a smaller amount of carbonaceous deposits.

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