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Dehydrogenation of Ethylbenzene over Vanadium Oxide-Loaded MgO Catalyst: Promoting Effect of Carbon Dioxide

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The dehydrogenation of ethylbenzene over a vanadium oxide-loaded MgO catalyst was investigated using carbon dioxide. The styrene yield in the presence of carbon dioxide was 2.5 times higher than that in the absence of carbon dioxide (argon atmosphere) at 823 K, indicating that carbon dioxide markedly promoted the dehydrogenation of ethylbenzene. At 873 K, the same catalyst afforded the highest styrene yield, 73.8% with a selectivity of 90.1%, in the presence of carbon dioxide. In order to elucidate the role of carbon dioxide in this reaction, characterization of the catalyst was carried out via methods such as temperature-programmed reduction, temperature-programmed reaction with carbon dioxide, and UV–visible, FT-IR, and XRD spectroscopies. Carbon dioxide behaved as an oxidant for the vanadium species, and the surface vanadium species were kept in a high oxidation state with carbon dioxide during the dehydrogenation reaction. Active phases of vanadium in the dehydrogenation reaction were believed to be V^{5+} species in V_2O_5 or $Mg_3V_2O_8$ on highly dispersed MgO. The reduced species, V^{4+} and V^{3+}, were less reactive sites for the dehydrogenation. © 2002 Elsevier Science (USA)

INTRODUCTION

Recently, increasing demand for styrene as one of the important monomers for synthetic polymers prompted several investigators to exploit a new process which reduces the cost of styrene production. Styrene monomer is commercially produced by means of the dehydrogenation of ethylbenzene using iron oxide as a catalyst, with an excess amount of superheated steam as a diluent and heat carrier (1). Since the product and effluent are rapidly cooled to avoid the polymerization of styrene, this process wastes a large amount of latent heat of vaporizing water. Currently, the development of a new energy-saving and more economical dehydrogenation process is of great importance.

The oxidative dehydrogenation of ethylbenzene (2–4) and short-chain alkanes (5–12) has received much attention; with this process, the reaction becomes exothermic and can be conducted at a low temperature. Several investigators have reported that a magnesium vanadate catalyst is the best catalyst for this reaction. Various physicochemical measurements, including X-ray diffraction (2–6), EXAFS (5), ESR (3, 12), UV–visible (9), Raman (10), IR (6–8), and temperature-programmed reduction (2), have been used to investigate the active species of the catalyst and the reaction mechanism, i.e., redox properties. Lopez-Cartes and coworkers reported that the oxidative dehydrogenation of propane proceeded with a redox cycle between $Mg_3V_2O_8$ and MgV_2O_4 (5), while on the other hand, Chang *et al.* reported a redox cycle between $Mg_3V_2O_8$ and Mg_2VO_4 during the dehydrogenation of ethylbenzene (2).

In this process, gas-phase oxygen is indispensable in maintaining the catalytic activity because the vanadium active species is reduced by the loss of a lattice oxygen of vanadium oxide with abstracting a hydrogen atom from alkanes. In the absence of oxygen, the catalytic activity sharply decreases with a decrease in the amount of available lattice oxygen (2, 11). However, in the presence of oxygen, the deep oxidation of alkanes to CO_x occurs more frequently, decreasing the desired olefin selectivity. Thus, this new dehydrogenation process cannot replace the process currently used without improving the olefin selectivity.

On the other hand, the use of carbon dioxide as a diluent instead of steam makes it possible to reduce the energy of the process and the cost of styrene production with high selectivity. If the present process using steam is replaced with the new process using carbon dioxide, the energy required for styrene production is calculated to be from 6.3×10^6 to 2.6×10^6 kJ/1000 kg of styrene (13). It is of additional interest that the gas that causes global warming, carbon dioxide, is effectively utilized in this chemical reaction.

One of the authors of the present study first reported that the dehydrogenation of ethylbenzene with an iron-loaded activated-carbon catalyst is promoted with carbon dioxide, and it was concluded that carbon dioxide acts as an oxidant in the redox cycle of iron oxide (14). Following this

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discovery, several investigators reported the use of carbon dioxide in the dehydrogenation of ethylbenzene with an iron-based catalyst (13, 15–17). However, to our knowledge, except for our previous report there has been no report about catalysts, other than those that are iron based, which are applicable to this new dehydrogenation process. In our previous study, the styrene yield in a carbon dioxide atmosphere was 1.27 times higher than that in an argon atmosphere at 823 K over a vanadium oxide-loaded activated-carbon catalyst. Among several supports of vanadium oxide, initial activity was not as high as that of activated carbon, but MgO exhibited the highest promoting effect of CO_2 (18). In this paper, we report on the remarkable promoting effect of carbon dioxide on the dehydrogenation of ethylbenzene over vanadium oxide-loaded MgO catalyst, and in order to elucidate the role of carbon dioxide in this reaction, characterizations of the catalyst were performed.

EXPERIMENTAL

Materials

All chemicals were used without further purification. Four kinds of magnesium oxides (Ube Materials Industries Ltd.), which have different surface areas, were used as supports. The catalyst was prepared by impregnating MgO with NH_4VO_3 according to following procedure. A certain amount of NH_4VO_3 was dissolved in an aqueous solution of oxalic acid (0.25 mol/L). To this solution MgO was added and it was allowed to stand overnight. Excess water was evaporated in vacuo, and the catalyst was calcined in air at 873 K for 4 h.

Catalytic Tests

The reaction was carried out with a fixed-bed flow-type quartz reactor operated at atmospheric pressure. A catalyst (50–150 mg) was placed at the center of the reactor using quartz glass wool plugs. The reaction was carried out at 773–873 K for 1–6 h. Ethylbenzene was fed (ca. 1.5 mmol/h) to the reactor by passing carbon dioxide or argon (30 ml/min) through the ethylbenzene saturator thermostated at 316 K. The effluent from the reactor was condensed in two traps containing heptane connected in a series. The condensed material was cooled externally in an ice water bath. The gaseous products were collected in a gas bag.

Reaction products (ethylbenzene, styrene, toluene, and benzene) were analyzed with a gas chromatograph equipped with a FID (Shimadzu GC14A), using a 3 mm × 3 m glass column packed with silicon SE-30. Carbon material balances were above 95% in all the cases. Analyses of gaseous products (CO, CO_2, and H_2) were carried out with a gas chromatograph equipped with a TCD (Shimadzu GC8A), using a 3 mm × 2.5 m stainless steel column packed with activated carbon.

$$\text{Conversion}\,(\%) = \left(1 - \frac{\text{EB recovered in traps in mol}}{\text{weight loss in EB saturator}/106}\right) \times 100\,(\%), \qquad [1]$$

where EB is ethylbenzene.

Catalyst Characterization

The surface area of the catalyst was measured by the BET method at 77 K using nitrogen as the adsorbate, with an automatic Micromeritics Gemini model 2375.

The temperature-programmed reduction was carried out with an automatic temperature-programmed desorption apparatus equipped with a quadrupole mass spectrometer as a detector (TPD-1-AT, BEL JAPAN INC.). Fresh catalyst (70 mg) was first treated with an O_2 (10 ml/min)/He (40 ml/min) mixture at 823 K for 1 h and cooled to 323 K in the same atmosphere. After replacing the O_2/He mixture with He, the catalyst was heated from 323 to 1073 K at a heating rate of 10 K/min under a stream of a H_2 (5 ml/min)/He (45 ml/min) mixture.

The catalysts treated under different conditions were analyzed by a Shimadzu UV-310PC UV–visible spectrophotometer with a diffuse reflectance mode. Fourier transform infrared (FT-IR) spectra were obtained by transmission mode with a JEOL JIR 7000. The catalyst was mixed with KBr and pressed into a thin pellet.

Powder X-ray diffraction was obtained with a Shimadzu model XRD-6000 diffractometer with monochromated Cu $K\alpha$ radiation.

The temperature-programmed reaction with carbon dioxide was carried out by means of an online quadrupole mass spectrometer (HAL 201, Hiden Analytical Ltd.), and carbon monoxide ($m/Z = 28$) was continuously monitored. The fresh catalyst was first reduced with hydrogen at 823 K for 1 h. After cooling to room temperature, the catalyst was heated from room temperature to 1073 K at a heating rate of 20 K/min under a stream of carbon dioxide.

RESULTS

Catalytic Tests

Table 1 shows the effect of the reaction temperature on the dehydrogenation of ethylbenzene supported on MgO and bulk vanadium oxide catalysts in the presence and absence of carbon dioxide. The numerals of YCO_2/YAr indicate the ratio of a styrene yield (reaction for 1 h) in the presence of carbon dioxide (CO_2/ethylbenezene = 45) to that in an argon atmosphere. For a vanadium oxide-loaded MgO (V/MgO) catalyst, styrene yield increased with an increase in reaction temperature and styrene selectivity was kept constant above 90% at these temperatures in both atmospheres. The styrene yield in the presence of carbon

TABLE 1

Effect of Reaction Temperature on Dehydrogenation of Ethylbenzene over Various Vanadium Oxide Catalysts[a]

			Under CO_2						Under Ar						
				ST yield						ST yield					
Entry	Catalyst	Temp (K)	EB Conv	%	mmol	ST sel (%)	CO mmol	H_2 (mmol)	EB Conv	%	mmol	ST sel (%)	CO (mmol)	H_2 (mmol)	YCO_2/YAr
1	V/MgO	773	17.2	15.8	0.26	92.2	0.32	0.00	8.8	8.3	0.13	95.2	0	0.11	1.90
2	V/MgO	823	59.1	53.8	0.74	91.1	1.09	0.05	22.7	21.9	0.32	96.5	0.1	0.43	2.46
3	V/MgO	823[b]	50.2	46.3	0.68	92.4	1.08	0.04	26.3	24.3	0.34	92.3	0	0.39	1.91
4	V/MgO	873	81.9	73.8	1.17	90.1	1.95	0.14	67.1	62.2	0.85	92.6	0.1	1.20	1.19
5	V_2O_5[c]	823	21.5	13.9	0.19	64.7	0.15	0.20	21.8	15.3	0.23	70.2	0.1	0.28	0.91

[a] Catalyst, 100 mg; V, 1.0 mmol/g of MgO; surface area, 144 m^2/g; reaction time, 1 h; W/F, 70 g of cat · h/mol.
[b] Catalyst was reduced with H_2 at 823 K for 6 h.
[c] Bulk vanadium oxide surface area less than 1 m^2/g.

dioxide was 2.5 times higher than that in an argon atmosphere at 823 K, showing the remarkable promoting effect of carbon dioxide. At 873 K, the V/MgO catalyst afforded the highest styrene yield (73.8%) in the presence of carbon dioxide. These results indicate that the V/MgO catalyst is an excellent catalyst for the dehydrogenation of ethylbenzene in the presence of carbon dioxide. Prior to the dehydrogenation of ethylbenzene, the catalyst was treated with hydrogen at 550°C for 6 h. The styrene yield in the presence of carbon dioxide decreased greatly, but that in the presence of argon increased slightly. When bulk vanadium(V) oxide was tested in the dehydrogenation reaction, only a low catalytic activity was observed in both atmospheres as compared to that with the V/MgO catalyst, and the promoting effect of carbon dioxide was not observed. Its effect was only observed on the V/MgO catalyst, in which vanadium species were highly dispersed throughout the MgO support. In Table 1 the amounts of CO and H_2 during the reaction are also shown. Within experimental errors, the amount of CO produced agreed with the amount of ethylbenzne converted in the runs under CO_2. However, in runs under Ar only H_2 was produced, with very small amounts of CO.

Figure 1 shows the effect of the vanadium-loading level on the styrene yield and selectivity in the presence and absence of carbon dioxide. A bare MgO exhibited very low styrene yield and selectivity in both atmospheres. In the presence of carbon dioxide, the styrene yield increased with an increase in the loading level from 0 to 1.0 mmol/g of MgO, but further increases in the loading level did not increase the styrene yield. On the other hand, in the argon atmosphere, the styrene yield monotonously increased with increases in the loading level. The styrene selectivity decreased above 1.5 mmol/g of MgO of the vanadium loading level in both atmospheres.

Figure 2 shows the effect of the contact time factor (W/F) on the dehydrogenation of ethylbenzene. In these experiments, W/F was changed by varying the amount of the catalyst charged under a constant ethylbenzene feed rate (1.5 mmol/h). With an increase in the contact time factor, the styrene yield increased, but the styrene selectivity gradually decreased even in the presence of carbon dioxide. This was due to an increase in the amount of by-products, especially benzene. However, the amounts of benzene and toluene did not exceed about 3% of styrene and carbon mass balance was over 95%. In the argon atmosphere, the styrene yield was low and it increased slightly with an increase in W/F.

Figure 3 shows the effect of specific surface areas of the catalyst on the dehydrogenation of ethylbenzene. The catalyst having a small surface area yielded a small amount of styrene in both atmospheres, and the yield did not depend on the atmosphere of the reaction. Styrene yield markedly increased with an increase in the surface area of the catalyst in the presence of carbon dioxide. However, in an argon atmosphere, the styrene yield did not increase with an increase in the surface area of the catalyst. The significant

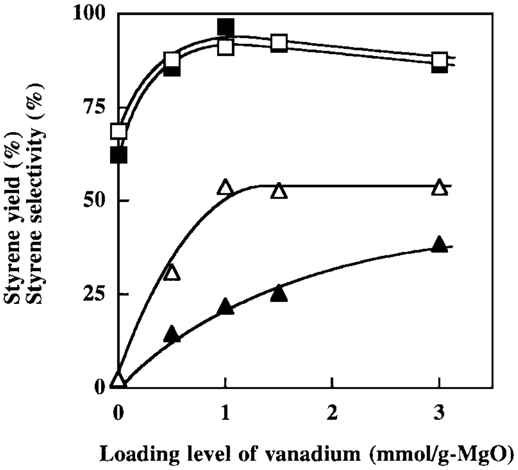


FIG. 1. Effect of loading level of vanadium on the styrene yield and the selectivity. Reaction temperature, 823 K; reaction time, 1 h; W/F, 70 g of cat · h/mol; catalyst, 100 mg. Ethylbenzene/CO_2 (mol/mol) = 45. Open symbols, under carbon dioxide flow; solid symbols, under argon flow; triangles, styrene yield; boxes, styrene selectivity.

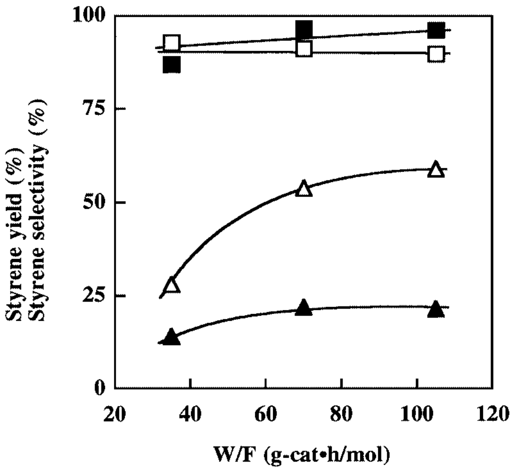


FIG. 2. Effect of W/F on the styrene yield and the selectivity. Reaction temperature, 823 K; reaction time, 1 h; V, 1.0 mmol/g of MgO. Keys are the same as shown in caption to Fig. 1.

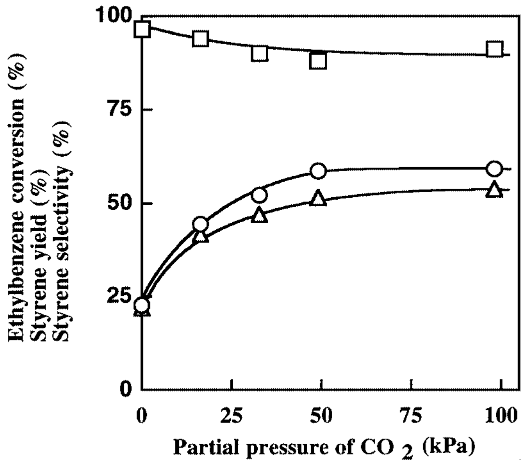


FIG. 4. Effect of partial pressure of carbon dioxide on the styrene yield and the selectivity. Reaction temperature, 823 K; reaction time, 1 h; W/F, 70 g of cat · h/mol; catalyst, 100 mg; V, 1.0 mmol/g of MgO. Ethylbenzene/CO_2 (mol/mol) = 45 at $P_{CO_2} = 98$ kPa; ethylbenzene/CO_2 (mol/mol) = 9 at $P_{CO_2} = 17$ kPa. (○) Ethylbenzene conversion, (△) styrene yield, (□) styrene selectivity.

promoting effect of carbon dioxide was only observed on the catalyst with a large surface area, in which vanadium species were highly dispersed on the MgO support.

The effect of partial pressure of carbon dioxide on the dehydrogenation of ethylbenzene was also investigated. The results are shown in Fig. 4. The partial pressure of carbon dioxide was changed by diluting carbon dioxide with argon, and the total flow rate was kept at 30 ml/min. In the absence of carbon dioxide, a low styrene yield was observed. However, by introducing a small amount of carbon dioxide into the reaction, the styrene yield markedly increased, and above a carbon dioxide partial pressure of 50 kPa (partial pressure of ethylbenzene = 3.3 kPa) the yield reached a level 2.5 times higher than that in the absence of carbon dioxide. Styrene selectivity decreased with an increase in styrene yield to give benzene and toluene as by-products.

Figure 5 shows the styrene yield and selectivity as a function of the reaction time at 823 K in the presence or absence of carbon dioxide. In the initial stage of the reaction, the styrene yield was very high in the presence of carbon dioxide (54.3%). However, when the reaction period increased, the styrene yield decreased gradually, and after 6 h, the styrene yield decreased to 37.3%. On the other hand, under an argon atmosphere, the initial styrene yield was low compared to the run under a carbon dioxide atmosphere, and the catalytic activity gradually increased to a small extent during the run for 6 h.

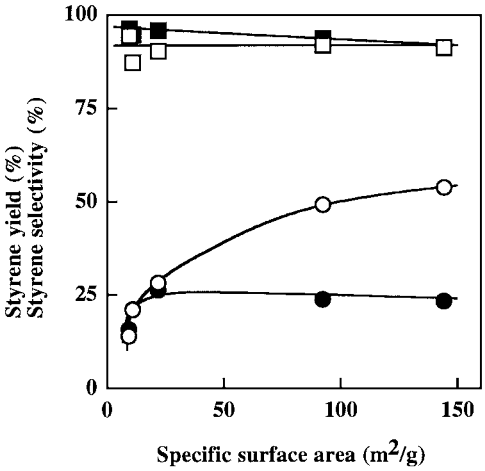


FIG. 3. Effect of specific surface area of catalyst on the styrene yield and the selectivity. Reaction temperature, 823 K; reaction time, 1 h; W/F, 70 g of cat · h/mol; catalyst, 100 mg; V, 1.0 mmol/g of MgO. Keys are the same as shown in caption to Fig. 1.

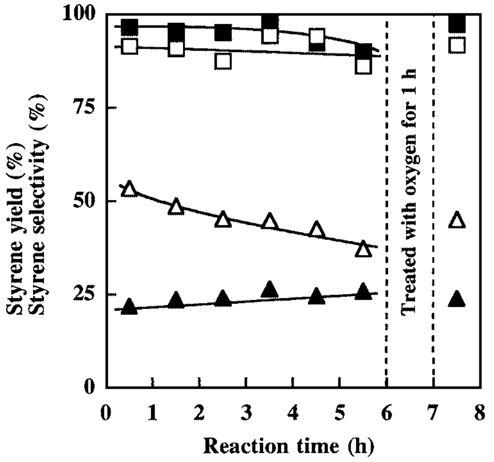


FIG. 5. Effect of time on stream on the styrene yield and the selectivity. Reaction temperature, 823 K; W/F, 70 g of cat · h/mol; catalyst, 100 mg; V, 1.0 mmol/g of MgO. Keys are the same as shown in caption to Fig. 1.

The styrene yield increased by air oxidation of the used catalyst after the reaction for 6 h in carbon dioxide, although the activity could not completely return to its initial level. On the other hand, the catalyst used under the argon atmosphere exhibited a lower activity after the oxidation of the catalyst.

During the treatment with oxygen (O_2–Ar, 5–15 ml/min), carbon dioxide and carbon monoxide were produced due to the oxidation of deposited carbon over the catalyst. Judging from the amount of produced CO_x, the coke deposition seemed to proceed more significantly in the reaction under a carbon dioxide atmosphere compared to that under an argon atmosphere.

Catalyst Characterization

Temperature-programmed reduction with hydrogen. The reducibility of the vanadium species over the V/MgO catalyst was measured by means of a temperature-programmed reduction with hydrogen. Figure 6a shows the effect of the vanadium-loading level, and Figure 6b shows the effect of the surface area of the catalyst on the reduction temperature of the vanadium species. Figure 6 (bottom) shows that the support MgO itself afforded a small H_2O peak at 525 K. This seems to be the absorbed water or hydroxy groups on MgO. On the other hand, in the V/MgO catalysts, the reduction peak appeared at 908 K, and the amount of water produced by the reduction increased with an increase in the loading level of vanadium from 0.5 to 1.5 mmol/g of MgO. However, at the higher loading level of 3.0 mmol/g of MgO, the reduction peak shifted to a high-temperature region compared to that of low-vanadium-loading catalysts, and multiple overlapping reduction peaks were observed. The reduction temperature shifted to a higher temperature region (1050 K) with a smaller amount of water when a smaller surface area catalyst (91 m^2/g) was examined (Fig. 6b).

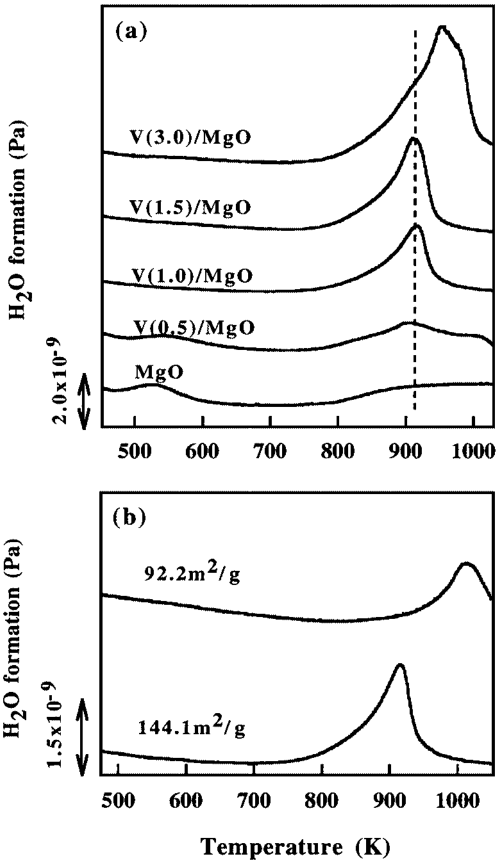


FIG. 6. Temperature-programmed reduction profiles for vanadium oxide-loaded MgO catalyst. (a) variations in the vanadium-loading level. Dotted line shows peak temperature of 910 K. (b) variation in the surface area. Catalyst, 70 mg; heating rate, 10 K/min; flow rate, He-45 ml/min, H_2-5 ml/min.

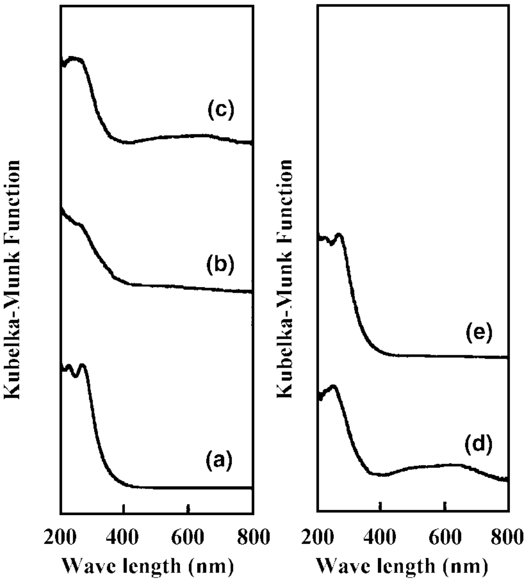


FIG. 7. UV–visible diffuse reflectance spectra of V(1.0)/MgO catalysts treated under various conditions: (a) fresh catalyst, (b) dehydrogenated under carbon dioxide flow at 823 K for 6 h, (c) dehydrogenated under argon flow at 823 K for 6 h, (d) fresh catalyst reduced with hydrogen at 823 K for 6 h, and (e) treated with carbon dioxide at 823 K for 6 h after the reduction with hydrogen.

UV–visible spectra. Figure 7a shows the UV–visible diffuse reflectance spectrum of the fresh V/MgO catalyst. The absorption band at 270 nm indicates the presence of tetrahedral V^{5+} species (9). After the dehydrogenation of ethylbenzene in the presence of carbon dioxide (Fig. 7b), this absorption was broadened and weakened. However, a weak and broad band with an absorption maximum between 500 and 700 nm appeared in the catalyst after the reaction under the argon atmosphere (Fig. 7c). Based on the fact that this broad band was observed in the hydrogen-reduced V/MgO catalyst (Fig. 7d), it is obvious that the reduction of the vanadium species proceeded during the dehydrogenation reaction in the argon atmosphere. On the other hand, the vanadium species was kept at a higher oxidation state in the carbon dioxide atmosphere. Figure 7e shows the spectrum of the catalyst treated with carbon dioxide for 6 h at 823 K after the reduction with hydrogen. The broad band assigned to the reduced vanadium species disappeared after being treated with carbon dioxide at 823 K, and distinct absorptions at 270 and 245 nm were observed.

IR spectroscopy. The FT-IR spectra of various V/MgO catalysts under different conditions are shown in Fig. 8. In these spectra, the contribution from MgO has been subtracted.

Figure 8a shows the FT-IR spectra of a fresh catalyst. This catalyst exhibited bands at 860 and 690 cm^{-1} due to $Mg_3V_2O_8$ (6–8). These bands became weak after the dehydrogenation reaction in the presence of carbon dioxide (Fig. 8b), and they disappeared after a dehydrogenation reaction in an argon atmosphere (Fig. 8c) and after the reduction with hydrogen (Fig. 8d). However, these bands appeared again after the treatment with carbon dioxide (Fig. 8e).

ESR spectroscopy. The ESR spectra of various V/MgO catalysts under different conditions were measured in order to investigate the changes in the oxidation state of the vanadium species. Details of the results have been described in a previous report (19). The ESR spectra demonstrated the oxidation capability of carbon dioxide for the vanadium species, and these results were consistent with the results of UV–visible and FT-IR spectra.

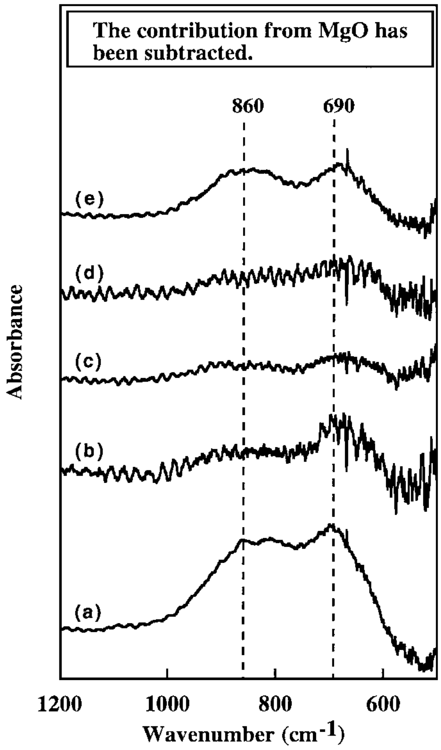


FIG. 8. FT-IR spectra of V(1.0)/MgO catalysts treated under various conditions. Conditions are the same as shown in caption to Fig. 7.

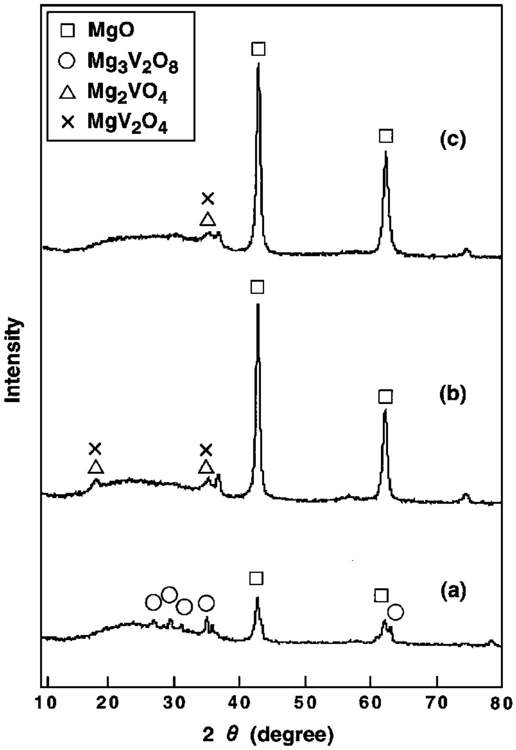


FIG. 9. XRD patterns of V(3.0)/MgO catalysts treated under various conditions: (a) fresh catalyst, (b) fresh catalyst reduced with hydrogen at 823 K for 6 h, and (c) treated with carbon dioxide at 823 K for 6 h after the reduction with hydrogen.

X-ray powder diffraction. Figure 9 shows the XRD patterns of the high-vanadium-loading catalyst. The fresh catalyst with the high-vanadium loading, 3.0 mmol of vanadium/g of MgO, showed weak diffraction peaks assigned to $Mg_3V_2O_8$ (Fig. 9a), although for the low-vanadium-loading catalyst only diffraction peaks assigned to MgO were observed. Figure 9b shows the diffraction patterns of the hydrogen-reduced catalyst. The diffraction peaks due to $Mg_3V_2O_8$ disappeared and new peaks assigned to a spinel-type phase, Mg_2VO_4 and/or MgV_2O_4, appeared. After the treatment with carbon dioxide, no significant changes in the diffraction patterns of the catalyst were observed (Fig. 9c).

Temperature-programmed reaction with carbon dioxide. In order to confirm the oxidation of the reduced vanadium species by carbon dioxide, a temperature-programmed reaction with carbon dioxide was carried out on the hydrogen-reduced V/MgO catalyst. The result is shown in Fig. 10. The catalyst afforded a small amount of carbon monoxide at a temperature between 700 and 900 K. The results clearly show that carbon dioxide oxidized the reduced vanadium species to a high-oxidation-state vanadium species and that carbon dioxide was reduced to carbon monoxide during the TPR study.

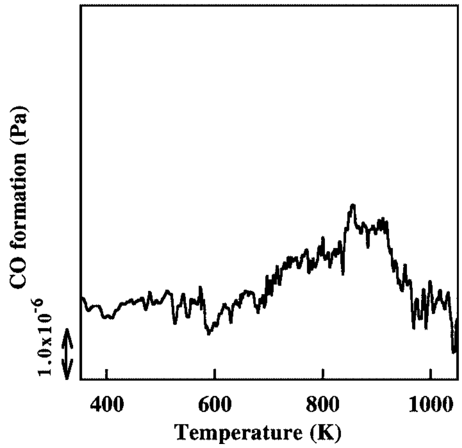
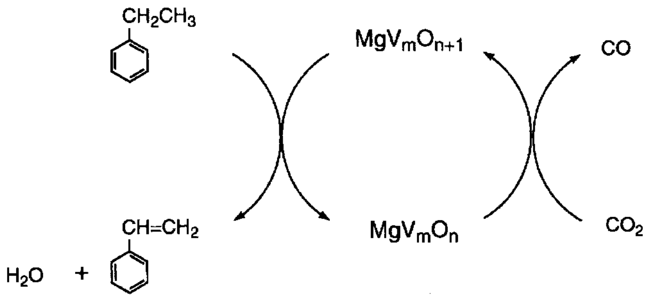


FIG. 10. Temperature-programmed reaction of the reduced vanadium oxide with carbon dioxide on V/MgO catalyst. Catalyst, 100 mg; *V*, 1.0 mmol/g of MgO; heating rate, 20 K/min; flow rate, CO_2-20 ml/min. H_2 reduction: 823 K, 2 h → Ar → CO_2 TPR.

DISCUSSION

In the previous paper, we showed that vanadium oxide loaded on activated carbon exhibited a high catalytic activity in the dehydrogenation of ethylbenzene under carbon dioxide (18). In the dehydrogenation of ethylbenzene over a V/MgO catalyst at 823 K, the styrene yield in the presence of carbon dioxide was 2.5 times higher than that in an argon atmosphere, indicating that the dehydrogenation reaction was markedly promoted by carbon dioxide. The results of various characterization techniques, including UV–visible, ESR, FT-IR, and CO_2-TPR spectra clearly indicate that lattice oxygen of the magnesium vanadate abstracts the hydrogen from ethylbenzene, that water and styrene are produced, and, consequently, that the vanadium species is reduced. In an argon atmosphere, the vanadium species is continuously reduced during the dehydrogenation reaction. On the other hand, in a carbon dioxide atmosphere, carbon dioxide can oxidize the reduced vanadium species, and the vanadium species is kept in a higher oxidation state (Scheme 1), resulting in a high styrene yield compared to that in an argon atmosphere.



SCHEME 1. Catalytic cycle of the dehydrogenation of ethylbenzene in the presence of carbon dioxide.

However, it seems difficult to keep the vanadium species at the initial high oxidation state throughout the reaction, since the oxidation capability of carbon dioxide is weaker than that of oxygen. This was supported by the ESR and XRD analyses. Based on the fact that no significant changes in the XRD patterns were observed between the reduced catalyst and the carbon dioxide-treated catalyst and that only a small amount of carbon monoxide was formed in the temperature-programmed reaction with carbon dioxide, it can safely be said that carbon dioxide can oxidize only the surface species of the reduced catalyst, while oxidation of the bulk of the reduced vanadium species cannot proceed with carbon dioxide. As shown in Table 1, formation of CO in the dehydrogenation under CO_2 is strong evidence of a redox cycle, although the possibility of hydrogenation of CO_2 with H_2 produced by the simple dehydrogenation cannot be ruled out. However, by such CO_2 hydrogenation the promoting effect of CO_2 in the dehydrogenation cannot easily be interpreted. Small amounts of formation of CO in Ar seem to be due to a reaction of deposited carbon with vanadium oxide.

With a decrease in W/F, the promoting effect of CO_2 measured by yield in CO_2/Ar decreased from 2.95 at W/F of 110 to 2.4 at W/F of 35, even in the presence of carbon dioxide, as seen in Fig. 2. On the other hand, conversion in Ar did not significantly change with a decrease in W/F. Such results can be interpreted as follows: The reoxidation rate of a reduced vanadium species with carbon dioxide is small. Thus, the reduction of the vanadium species proceeds faster than the reoxidation of the reduced vanadium species at a higher space velocity, resulting in a decrease in the number of active sites and the apparent promoting effect of carbon dioxide.

Table 2 shows the results of thermochemical calculations of the oxidation of the lower-valency-state vanadium oxides with carbon dioxide at 800 and 900 K (20). From the values of ΔG in the respective reactions, it seems it would be difficult for carbon dioxide to oxidize the bulk vanadium oxide of a lower valency state, although it may be possible for some of this reaction to occur. However, loading it onto the support may alter the thermochemical parameters of vanadium oxide in a mixed oxide. Especially over a MgO

TABLE 2

Oxidation of Lower Valent Vanadium Oxide with Carbon Dioxide

	ΔG (kJ/mol of V)	
Reaction	800 K	900 K
$VO_2 + 1/2\ CO_2 \rightarrow 1/2\ V_2O_5 + 1/2\ CO$	78.27	78.72
$1/2\ V_2O_3 + CO_2 \rightarrow 1/2\ V_2O_5 + CO$	114.35	113.81
$VO + 3/2\ CO_2 \rightarrow 1/2\ V_2O_5 + 3/2\ CO$	73.35	72.27
$1/2\ V_2O_3 + 1/2\ CO_2 \rightarrow VO_2 + 1/2\ CO$	36.08	35.09
$VO + CO_2 \rightarrow VO_2 + CO$	−4.92	−6.45
$VO + 1/2\ CO_2 \rightarrow 1/2\ V_2O_3 + CO$	−41.00	−41.54

support, the strong interaction between acidic vanadia and basic magnesia results in the formation of mixed oxides. UV–visible, ESR, and CO_2-TPR experiments strongly suggest that carbon dioxide can oxidize the lower-valency-state vanadium oxide to higher valency oxides.

Considering that the promoting effect of carbon dioxide was observed on the V/MgO catalyst with a large surface area but not observed on bulk V_2O_5, the oxidation of lower-valency-state vanadium species with carbon dioxide may occur only in mixed oxides highly dispersed on magnesium oxide. Therefore, even if the bulk lower-valency-state vanadium oxides could not be oxidized, complex oxides of magnesium vanadate could be oxidized to a higher valency state with carbon dioxide.

According to the results shown in Fig. 5, in a carbon dioxide atmosphere, the styrene yield decreased with an increase in the reaction period due to the coke deposition and increases in the lower-valency-state vanadium species. On the other hand, in an argon atmosphere, the initial styrene yield was very low and the styrene yield slightly increased with an increase in the reaction period. Presumably, under an argon atmosphere, the dehydrogenation reaction proceeds on the site different from that of the redox cycle with higher-valency-state oxides and lower-valency oxides. Therefore, after the available active oxygen in the lattice of the catalyst was consumed in the initial period, the catalytic activity was not lost and the catalyst continued to produce a low yield of styrene.

Ishida *et al.* reported that the reduction of a vanadium oxide-loaded Al_2O_3 catalyst creates a new Lewis acid site assigned to the reduced vanadium species (21). The fact that the styrene yield increased and styrene selectivity decreased with the hydrogen reduction of the V/MgO catalyst in an argon atmosphere (Table 1) leads to the conclusion that the active site changed and a new acidic site was created by the reduction during the dehydrogenation of ethylbenzene in the argon atmosphere, resulting in a slight increase in the styrene yield with an increase in the reaction period. The active site in a carbon dioxide atmosphere would seem to be the redox site and that in an argon atmosphere a weak acid site of magnesium vanadate. The active sites differ according to the atmosphere.

It is well-known that various magnesium vanadates can be formed and that among them meta-MgV_2O_6, pyro-$Mg_2V_2O_7$, and ortho-$Mg_3V_2O_8$ are the stable compounds (10). According to Chang *et al.*, the reducibility of these vanadates differs and the order is reported to be $Mg_3V_2O_8 > MgV_2O_6 > Mg_2V_2O_7$. Furthermore, in the dehydrogenation of ethylbenzene in the presence of oxygen, $Mg_3V_2O_8$ is active and selective; on the other hand, MgV_2O_6 and $Mg_2V_2O_7$ are active but nonselective toward styrene formation (2).

In our study, differences in the reduction temperature of the vanadium species with hydrogen were observed (Fig. 6). For the low-vanadium-loading catalyst ($V \leqq 1.5$ mmol/g of MgO), a single and low-temperature peak was observed, but for the high-vanadium-loading catalysts ($V = 3.0$ mmol/g of MgO), overlapping peaks at higher temperatures were detected. On the low-loading catalyst, an isolated VO_4 species forming a $Mg_3V_2O_8$ structure exists with a high dispersion over the MgO support. On the higher loading case, in addition to this species, polymeric V^{5+} species with bridging V–O–V oxide ions forming MgV_2O_6 and $Mg_2V_2O_7$ structures coexist (10, 22), resulting in a decrease in the styrene selectivity over a V(3.0)/MgO catalyst. It is believed that the styrene yield did not increase above the loading level of 1.0 mmol/g of MgO since the isolated VO_4 species did not increase above this loading level in the presence of carbon dioxide.

This interpretation can be applied to the behavior shown in Fig. 3. For the catalyst with a small surface area, the dispersion of vanadium species lowered, and MgV_2O_6 and/or $Mg_2V_2O_7$ were formed. Therefore, this catalyst did not afford the promoting effect of carbon dioxide.

Only vanadium species on a high-surface-area MgO exhibited high catalytic activity and large promoting effect of CO_2. Bulk $Mg_3V_2O_8$, and MgV_2O_6, and $Mg_2V_2O_7$ compound oxides did not show high catalytic activity and promoting effect of CO_2 in the dehydrogenation of ethylbenzene and 3-ethylbipheny, although the surface areas of these oxides were small (23). Catalytically active phase of V_2O_5 loaded on a high-surface-area MgO, in the dehydrogenation of ethylbenzene under CO_2, is difficult to determine whether $Mg_3V_2O_8$ or highly dispersed V_2O_5 on MgO. Results from IR spectra show the possibility of redox cycles of $Mg_3V_2O_8$ and Mg_2VO_4, but in the XRD, it is observed that Mg_2VO_4 was not oxidized into $Mg_3V_2O_8$. UV and ESR results only afforded redox cycles of V^{5+} and V^{4+}. Thus at present, we could safely conclude that the active phase of CO_2-promoted dehydrogenation of ethylbenzene would be V^{5+} species in V_2O_5 or $Mg_3V_2O_8$ on highly dispersed MgO.

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