Dehydrogenation of isopropylbenzene with vanadium-oxide-loaded activated carbon catalyst in the presence of carbon dioxide

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Dehydrogenation of isopropylbenzene to α-methylstyrene was carried out using various supported metal oxide catalysts in the presence of carbon dioxide. An activated carbon-supported vanadium oxide catalyst afforded a high activity in carbon dioxide atmosphere: the α-methylstyrene yield in carbon dioxide atmosphere was two times greater than that in an argon atmosphere at 723 K. In order to investigate the role of carbon dioxide in this reaction, we carried out temperature-programmed reduction (TPR) studies using both fresh and used catalysts. The TPR profiles clearly indicate that carbon dioxide could keep the surface of vanadium oxide at a high oxidation state.

Keywords: dehydrogenation, oxidative dehydrogenation, cumene, α-methylstyrene, vanadium oxide, activated carbon, temperature-programmed reduction

1. Introduction

α-methylstyrene (MST) is an important monomer in the petrochemical industry. Industrially, MST is obtained as a by-product of oxidation of isopropylbenzene (IPB) to give phenol and acetone. Recently a new MST-production process has been investigated. Bradely et al. reported on a cracking reaction of IPB with an alumina-supported gallium catalyst [1]. The cracking behavior of IPB has been used to evaluate Brønsted acid catalysts [2,3]. In this reaction MST was obtained as a by-product. On the Brønsted acid site, benzene was a primary product; MST was obtained as a major product in the radical reaction [4].

Few investigations of the dehydrogenation of IPB have been published. Miura et al. reported on the use of a commercial catalyst for the dehydrogenation of ethylbenzene in the reaction with IPB. The rate constant for the dehydrogenation of IPB was two times larger than that of ethylbenzene, in the temperature range of 798–923 K [5]. Uranium-oxide-containing catalyst was reported to be active in the dehydrogenation of ethylbenzene to give a styrene yield of 38% at 793 K, and IPB to give a MST yield of 66% at 753 K under optimum conditions [6].

One of the authors of this study recently reported on the catalytic dehydrogenation of ethylbenzene, isobutane, and ethane in the presence of carbon dioxide. Iron-oxide-loaded activated carbon [7,8], vanadium-oxide-loaded activated carbon [9] and gallium oxide [10,11] exhibited higher catalytic activities in the runs in a carbon dioxide atmosphere as compared to the run in an inert gas (argon) atmosphere. Recently much attention has been paid to the use of carbon dioxide as a promoting agent for the dehydrogenation of ethylbenzene [12] and several alkanes [13,14]. However, none of these studies clarified the promoting effect of carbon dioxide on the catalytic activities.

In this paper, we report on the promoting effect of carbon dioxide on the dehydrogenation of IPB over a vanadium-oxide-loaded activated carbon (V/AC) catalyst. Our aim was to learn about the promoting effect of carbon dioxide on the dehydrogenation of various organic substrates.

2. Experimental

2.1. Materials

All chemicals were purchased from commercial sources and used without any further purification. Activated carbon (Wako Pure Chemicals granular, 948 m^2/g), Al_2O_3 (Sumitomo Chemical Industries, 126.3 m^2/g), MgO (Ube Chemical Industries, 66.0 m^2/g), and SiO_2 (Wako Pure Chemicals, 143.0 m^2/g) were used as supports. The supported catalysts were prepared by impregnating an aqueous solution of $Fe(NO_3)_3{\cdot}H_2O$, $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$, $Cr(NO_3)_3{\cdot}9H_2O$, $RuCl_3{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, $Mn(NO_3)_2{\cdot}6H_2O$, $Ga(NO_3)_3{\cdot}8H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $LiNO_3$ on the support. Only NH_4VO_3 was dissolved in an aqueous solution of oxalic acid. After the impregnation, which had an overnight duration, the excess water was evaporated to dryness under a vacuum. The dried catalysts were calcined at 873 K for 4 h in air, except for the activated carbon-supported catalyst.

2.2. Procedure

The reaction was carried out in an ordinary flow-type reactor (stainless-steel tube) in 1 atm pressure. Details of the reaction were reported previously [7].

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2.3. Analyses of catalysts

Surface areas of the catalysts were measured by the BET method with an automatic Micromeritics Gemini model 2375.

Powder X-ray diffraction was obtained with a Shimadzu model X-6000 diffractometer, irradiated by monochromated Cu Kα line.

Temperature-programmed reaction (TPR) was carried out using a similar reactor, and the effluent was introduced into a quadrupole mass spectrometer (Hiden model HAL 201) equipped with a differential vacuum intake port. The fresh or reacted catalyst was heat-treated at 373–1173 K at a heating rate of 20 K/min under a stream of hydrogen. Methane ($m/z = 15$), H_2O ($m/z = 18$), and C_2H_4 ($m/z = 28$) were continuously monitored.

3. Results and discussion

3.1. Catalytic activities of various metal-oxide-loaded catalysts

Table 1 shows catalytic activities during the dehydrogenation of IPB with various metal-oxide-loaded activated carbon catalysts. The activity was compared by cumulative yield of MST during a run for 2 h. Compared to the dehydrogenation of ethylbenzene, a much higher conversion of IPB was observed at a low temperature of 723 K [7]. The iron-oxide-loaded activated carbon catalyst exhibited the highest MST yield among all catalysts that were tested. This catalyst, however, did not exhibit the promoting effect of carbon dioxide.

In the dehydrogenation of ethylbenzene with the same catalyst, carbon dioxide behaved as an oxidant for iron oxide. The surface iron oxide was kept at a higher oxidation state during the dehydrogenation in the presence of carbon dioxide, resulting in a higher styrene yield as compared to that in an argon atmosphere. This effect was revealed by XRD studies [7]. However, in the dehydrogenation of IPB at 723 K, XRD studies on the catalyst exhibited the same patterns in fresh and used catalysts in both atmospheres.

Vanadium-oxide-, molybdenum-oxide-, and chromium-oxide-loaded activated carbon catalysts showed moderate catalytic activities for the dehydrogenation of IPB. However, conversions of IPB over these catalysts were smaller than those produced by iron-oxide-loaded catalyst. Among these catalysts, only the V/AC catalyst increased the conversion of IPB in the presence of carbon dioxide atmosphere. All other catalysts did not exhibit the promoting effect of carbon dioxide.

In table 2, the effect of several supports of vanadium-oxide-loaded catalyst on the dehydrogenation of IPB is summarized together with surface area. Vanadium-oxide-loaded Al_2O_3, SiO_2, and MgO catalysts, which have moderate surface areas, exhibited lower conversions and selectivities as compared to the V/AC catalyst in both atmospheres, and the promoting effect of carbon dioxide was not observed over these catalysts. This effect was observed only on the V/AC catalyst. Consequently, detailed studies on the V/AC catalyst were carried out.

Table 1
Dehydrogenation of isopropylbenzene with various metal-oxide-loaded activated carbon catalysts.[a]

Run	Catalyst	IPB conv. (%)	MST yield (%)	MST selec. (%)
1	None	0.3	0.2	71.2
2	AC	2.6	2.0	76.1
3	Fe(0.5)/AC	28.0	26.3	93.8
4	Fe(0.5)/AC[b]	30.3	27.9	92.3
5	V(0.5)/AC	24.4	21.5	88.3
6	V(0.5)/AC[b]	12.9	11.3	87.3
7	Mo(0.5)/AC	21.2	20.2	95.1
8	Mo(0.5)/AC[b]	22.8	20.6	90.6
9	Cr(0.5)/AC	21.6	19.2	88.9
10	Cr(0.5)/AC[b]	24.1	18.0	74.5
11	Ru(0.5)/AC	14.2	13.5	91.9
12	Co(0.5)/AC	13.6	12.9	94.8
13	Mn(0.5)/AC	12.9	12.8	98.8
14	Ga(0.5)/AC	9.8	7.8	80.0
15	Ce(0.5)/AC	9.1	8.4	92.2
16	Ni(0.5)/AC	8.3	5.9	71.7
17	Li(0.5)/AC	4.2	4.2	98.8
18	V(1.5)/AC	31.3	28.3	90.6
19	V(1.5)/AC[b]	25.2	22.5	89.1
20	V(1.5)/AC[c]	36.4	32.0	88.1
21	V(1.5)/AC[b,c]	31.5	28.5	90.5

[a] Catalyst 50 mg, loading level of metal oxide 0.5–1.5 mmol/g-carbon, reaction time 2 h, reaction temperature 723 K, $W/F = 50$ g-cat h/mol.
[b] Reaction under argon atmosphere.
[c] Reaction temperature 748 K.

Table 2
Effect of support of vanadium-oxide-loaded catalyst on the dehydrogenation of IPB.[a]

Entry	Catalyst (surface area)	Under carbon dioxide					Under argon			
		Conv. (%)	Yield (%)	Selec. (%)	CO[b]	H_2[b]	Conv. (%)	Yield (%)	Selec. (%)	H_2[b]
1	V/AC (762.6 m^2/g)	33.7	30.2	89.8	1.15	0.1	25.5	22.5	89.1	1.12
2	V/Al_2O_3 (81.0 m^2/g)	18.0	13.6	75.9	1.10	~0	15.0	10.3	68.3	1.15
3	V/SiO_2 (87.0 m^2/g)	12.5	8.7	70.0	1.20	~0	13.8	8.7	63.4	1.20
4	V/MgO (52.7 m^2/g)	6.7	6.4	96.5	1.10	~0	4.3	4.1	94.5	1.15

[a] Catalyst 100 mg, V 1.5 mmol/g-support, reaction time 2 h, reaction temperature 723 K, $W/F = 50$ g-cat h/mol. Conv. – isopropylbenzene conversion, Yield – α-methylstyrene yield, Selec. – α-methylstyrene selectivity.
[b] CO, H_2 mol/mol IPB converted.

3.2. Effect of reaction conditions on the dehydrogenation of IPB over the V/AC catalyst

The effect of loading level of vanadium oxide on the dehydrogenation of IPB is shown in figure 1. With increasing vanadium-loading level, from 0.5 to 1.5 mmol/g-AC, the MST yield increased from 19.0 to 28.3% in the presence of carbon dioxide. With further increase in the loading level to 5.0 mmol/g-AC, the MST yield unexpectedly decreased slightly. Similar behavior was seen in the dehydrogenation of ethylbenzene with the same catalyst at 823 K [9]. Such decrease in the conversion at a higher loading level can be ascribed to the decrease in the surface area of the catalyst. Although with the iron-oxide-loaded catalyst the optimum loading level was as low as 0.5 mmol Fe/g-AC, a much larger amount of vanadium is needed to obtain high activity in the dehydrogenation of IPB. Under an argon atmosphere, an increase in the vanadium loading level from 0.5 to 1.5 mmol/g-AC increased the MST yield from 11.3 to 22.5%. These values are smaller than those observed in the run under carbon dioxide, indicating that the promoting effect of carbon dioxide did not change with the loading level of vanadium.

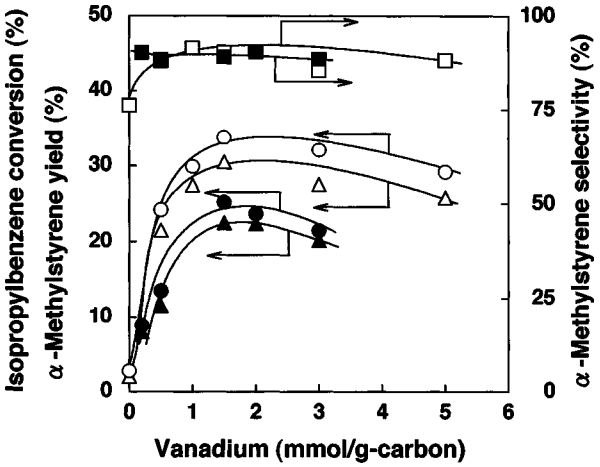

Figure 1. Effect of loading level of vanadium on the IPB conversion, MST yield and selectivity. Reaction temperature 723 K, reaction time 2 h, $W/F = 50$ g-cat h/mol, catalyst 50 mg. Run under CO_2: (□) MST selectivity, (○) IPB conversion and (△) MST yield. Run under Ar: (■) MST selectivity, (●) IPB conversion, and (▲) MST yield.

Figure 2(a) shows the effect of reaction temperature on the dehydrogenation of IPB in the presence of carbon dioxide. A maximum conversion of IPB and a maximum yield of MST were obtained at 748 K in a carbon dioxide atmosphere. Further increase in the reaction temperature decreased both the conversion and yield with decreasing MST selectivity. The decrease in the selectivity could partly be attributed to the increase in the by-products benzene, toluene, styrene, and ethylbenzene. Total selectivity of these by-products increased from 2% at 748 K to 7% at 823 K.

Figure 2(b) shows the temperature dependency of the dehydrogenation of IPB in an inert atmosphere of argon. IPB conversion increased steadily with increasing reaction temperature whereas yield and selectivity to MST decreased above 773 K. Decreases in the yield and selectivity could be attributed to the increase in the coke deposition in addition to the above by-products. This was confirmed by the decrease in the amounts of recovered products, from 97.3% at 748 K to 84.5% at 823 K. A comparison of figure 2 (a) and (b) showed temperature dependence differences in the dehydrogenation of IPB on the V/AC catalyst in carbon dioxide and argon atmosphere. Under a carbon dioxide atmosphere, IPB conversion did not increase above 748 K, indicating a strong interaction between the catalyst surface and carbon dioxide, which might have decreased the adsorption of IPB on the catalyst surface. However, in an argon atmosphere such interaction could not occur; consequently IPB conversion increased in proportion to the rise in the reaction temperature. The promoting effect of carbon dioxide decreased at a higher reaction temperature.

An alternate interpretation for the above phenomena could be as follows: In a carbon dioxide atmosphere, a rapid deactivation of the catalyst occurred at a temperature range of 750–850 K because of the initial high activity of the catalyst. Consequently, the cumulative conversion and yield for 2 h decreased with increasing reaction temperature

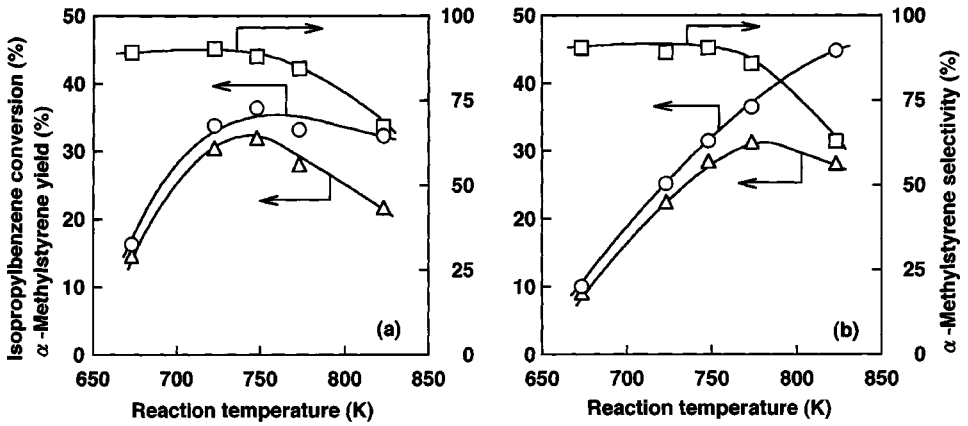

Figure 2. Effect of reaction temperature on the IPB conversion, MST yield and selectivity: (a) under carbon dioxide flow and (b) under argon flow. Reaction time 2 h, $W/F = 50$ g-cat h/mol, catalyst 50 mg, V 1.5 mmol/g-carbon. (□) MST selectivity, (○) IPB conversion, and (△) MST yield.

in a carbon dioxide atmosphere. In an argon atmosphere, the rapid deactivation of the catalyst was not significant due to the low activity. Thus, conversion of IPB increased steadily with an increase in the reaction temperature. However, such possibility seems to be unlikely.

The effect of contact time (W/F) on the dehydrogenation of IPB is shown in figure 3. With an increase in the contact time, IPB conversion and MST yield increased; it was accompanied by a decrease in MST selectivity. The MST selectivity decreased due to the thermal decomposition of IPB and MST to by-products (benzene, toluene, ethylbenzene, and styrene) over a long contact time.

The effect of reaction time on the dehydrogenation of IPB in both carbon dioxide and argon atmosphere was examined (figure 4). A rapid deactivation of the catalyst performance was observed in both atmospheres. During the experiments, much higher IPB conversion and MST yield were observed in the initial stage of the reaction under a carbon dioxide atmosphere, where IPB conversion and IPB yield reached 41.4 and 36.7%, respectively. Under an argon atmosphere, IPB conversion and MST yield were 30.5 and 26.9%, respectively. After a reaction period of 5 h, the MST yield decreased to 11.1% in carbon dioxide and 14.9% in argon atmosphere. A rapid decrease in the MST yield was observed in carbon dioxide atmosphere. This could be in part due to the fact that a larger amount of IPB was dehydrogenated in carbon dioxide than in argon. When the dehydrogenation rate was plotted against the amount of reacted IPB, similar decay curves were seen for the reactions in both atmospheres. Such decrease in the reaction rate during the reaction could be ascribed to the carbon deposition and changes in the oxidation state of vanadium species.

At the initial stage of the reaction vanadium oxide on activated carbon would be kept in a higher oxidation state due to the oxidation capability of CO_2. However, the oxidation capability of CO_2 is not sufficient at 450–475 °C. Therefore, during the reaction deactivation proceeded in addition to carbon deposition.

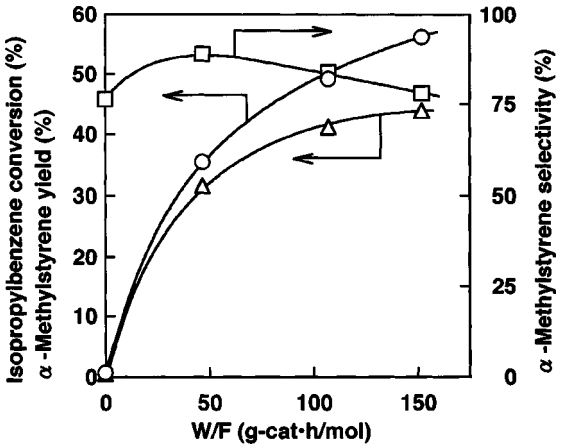

Figure 3. Effect of W/F on the IPB conversion, MST yield and selectivity under carbon dioxide flow. Reaction temperature 748 K, reaction time 2 h, V 1.5 mmol/g-carbon. (□) MST selectivity, (○) IPB conversion, and (△) MST yield.

3.3. Characterization of catalyst

In order to understand the oxidation state of vanadium oxide, an XRD measurement was carried out. Despite the vanadium loading level, from 0.5 to 1.5 mmol/g-AC, no or very weak diffraction peaks were observed. As is well known, vanadium oxide on a support with a large surface area would be dispersed to monolayer [15]. When the loading level was increased above 2.0 mmol/g-AC, distinct XRD patterns were observed. Further studies were carried out with a catalyst of 3.0 mmol/g-AC. The fresh catalyst pre-treated at 973 K showed diffraction peaks assigned to V_2O_3, indicating that penta-valent vanadium oxide was reduced to tri-valent state during the impregnation in oxalic acid solution and the heat treatment with carbon dioxide. After the dehydrogenation in carbon dioxide and an argon atmosphere, no significant changes in the diffraction patterns of the catalyst were observed. Thermodynamically at these temperature ranges, oxidation of V_2O_3 with carbon dioxide is not favorable; thus these results are valid.

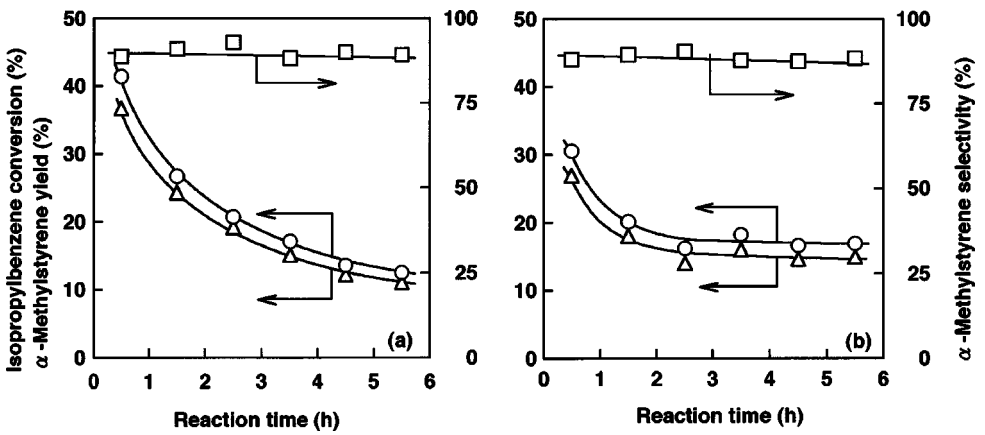

Figure 4. Effect of reaction time on the IPB conversion, MST yield and selectivity: (a) under carbon dioxide flow and (b) under argon flow. Reaction temperature 723 K, $W/F = 50$ g-cat h/mol, catalyst 50 mg, V 1.5 mmol/g-carbon. (□) MST selectivity, (○) IPB conversion, and (△) MST yield.

3.4. Temperature-programmed desorption (TPD) and reduction (TPR)

TPD and TPR studies on V/AC catalysts were carried out to obtain detailed information of the role of carbon dioxide. TPD profiles of various V/AC catalysts after different treatments are shown in figure 5. Activated carbon support after heat treatment in carbon dioxide for 10 min at 973 K afforded a small amount of carbon monoxide desorption above 923 K, but desorption of carbon dioxide was not observed. When the V/AC catalyst was treated with carbon dioxide at 973 K for 10 min, desorption of a larger amount of carbon monoxide was observed together with a small desorption of carbon dioxide at a slightly lower temperature. The desorption of carbon monoxide and carbon dioxide on the V/AC catalyst seems to be the reaction of vanadium oxide with carbon support. After dehydrogenation of IPB was run for 2 h, TPD was carried out. In both carbon dioxide and argon atmosphere, desorption of carbon monoxide was observed at the slightly lower temperature of 880 K as compared to TPD with the fresh catalyst. No carbon dioxide desorption was observed in either case. Desorption of carbon monoxide at a lower temperature seems to be the reaction of vanadium oxide with coke formed on the catalyst. No significant differences in the desorption profiles between the reaction in carbon dioxide and in argon were observed.

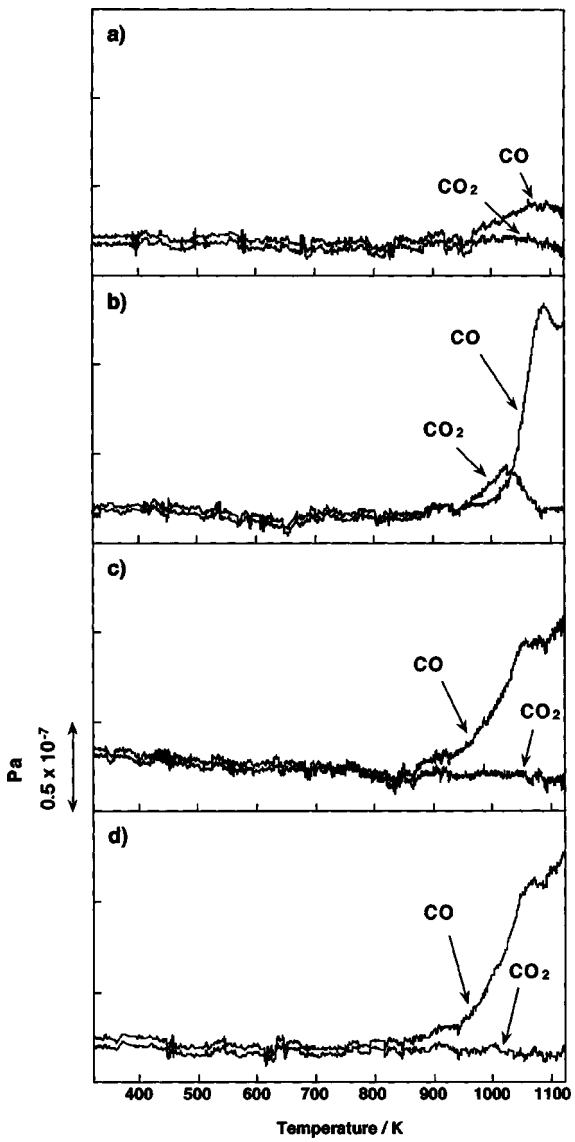

Figure 5. Temperature-programmed desorption spectra of V/AC catalysts. Heating rate 20 K/min, sweep gas argon = 20 ml/min, catalyst 100 mg. (a) Activated carbon was pre-treated at 973 K for 10 min in carbon dioxide atmosphere; (b) V(1.5)/AC catalyst was pre-treated at 973 K for 10 min in carbon dioxide atmosphere; (c) after dehydrogenation of IPB in carbon dioxide atmosphere at 723 K for 2 h; and (d) after dehydrogenation of IPB in argon atmosphere at 723 K for 2 h.

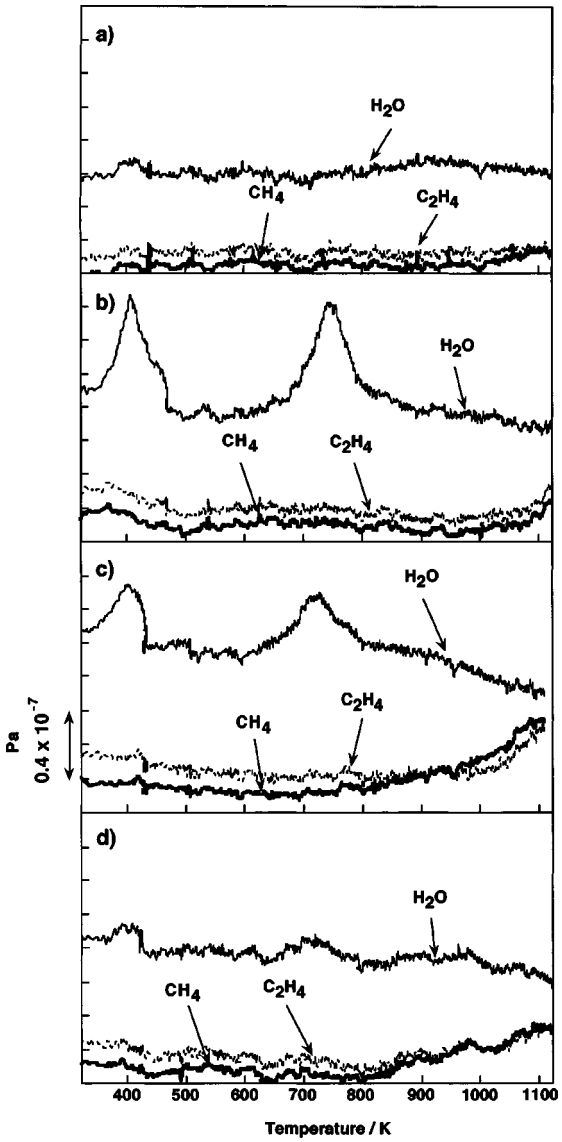

Figure 6. Temperature-programmed reduction spectra of V/AC catalysts. Heating rate 20 K/min, sweep gas hydrogen = 20 ml/min, catalyst 100 mg. (a) Activated carbon was pre-treated at 973 K for 10 min in carbon dioxide atmosphere; (b) V(1.5)/AC catalyst was pre-treated at 973 K for 10 min in carbon dioxide atmosphere; (c) after dehydrogenation of IPB in carbon dioxide atmosphere at 723 K for 2 h; and (d) after dehydrogenation of IPB in argon atmosphere at 723 K for 2 h.

In order to investigate the role of carbon dioxide in the dehydrogenation of IPB with the V/AC catalyst, we carried out further studies of TPR with hydrogen. The results are shown in figure 6. The activated carbon support yielded no product except for a very small desorption of adsorbed H_2O at 410 K. The fresh catalyst treated with carbon dioxide afforded two distinct peaks of H_2O formation at 410 and 723 K. Similar profiles were seen in the catalyst after dehydrogenation of IPB in a carbon dioxide atmosphere. However, the catalyst that reacted under an argon atmosphere exhibited only slight desorption of H_2O at both temperatures. Desorption of CH_4 and C_2H_4 were seen after the dehydrogenation of IPB in carbon dioxide and the argon atmosphere, indicating the coke formation on the vanadium oxide. The fact that H_2O formation in the TPR study disappeared after dehydrogenation in the argon atmosphere indicates a reduction of surface of the vanadium oxide during the reaction in the argon atmosphere. The TPR study after the reaction in carbon dioxide atmosphere afforded two reduction peaks of vanadium oxide. This clearly indicates that carbon dioxide keeps vanadium oxide at a high oxidation state during the reaction. A decrease in the amount of H_2O formed in the TPR of the used catalyst indicates that even in a carbon dioxide atmosphere, gradual reduction in the vanadium oxide did occur.

These results indicate that carbon dioxide acts as a weak oxidant for the vanadium catalyst. As mentioned above, XRD spectra did not show the existence of vanadium oxide with a higher oxide state in the bulk structure; however, the surface of V_2O_3 would be covered with V_2O_5 or V_2O_4 species.

4. Conclusion

An activated-carbon-supported vanadium oxide catalyst exhibited a high MST yield in the presence of carbon dioxide. The MST yield markedly increased by introducing carbon dioxide in this reaction with this catalyst.

X-ray diffraction analyses of the V/AC catalyst revealed that the bulk of the vanadium species comprised V_2O_3 at a high loading level and this species did not change before and after the reaction in both atmospheres. However, in the TPR studies differences in the intensities of reduction peaks were observed. The fresh catalyst and the tested catalyst in carbon dioxide atmosphere gave distinct reduction peaks, but the catalyst tested in the argon atmosphere did not give these peaks. This clearly indicated that carbon dioxide could keep the surface of vanadium oxide at a high oxidation state, resulting in the high MST yield in the carbon dioxide atmosphere.

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