Oxidation Capability of Carbon Dioxide in the Dehydrogenation of Ethylbenzene over Vanadium Oxide-Loaded MgO Catalyst

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(Received February 1, 2000; CL-000108)

Carbon dioxide could oxidize the reduced vanadium oxide species on MgO and keep vanadium species at a high oxidation state, during the dehydrogenation of ethylbenzene to styrene under carbon dioxide, giving a markedly high yield and selectivity of styrene.

In order to reduce energy consumption in olefin production, the oxidative dehydrogenation of alkanes has recently received much attention; with this process, the reaction becomes exothermic and can be operated at a low temperature.[1-3] Several investigators have reported that vanadium oxide-magnesia complex oxide catalyst is the best catalyst for the oxidative dehydrogenation of ethylbenzene and that the reaction proceeds with a redox cycle of vanadium oxides between V^{4+} and V^{5+} in the presence of oxygen.[1-3]

One of the present authors first reported that the dehydrogenation of ethylbenzene with an iron-loaded activated carbon catalyst is promoted with carbon dioxide, concluding that carbon dioxide acts as an oxidant, with the redox cycle of iron oxide being maintained at a higher oxidation state.[6] Several investigators have reported the use of carbon dioxide in the dehydrogenation of ethylbenzene.[7,8] Carbon dioxide has been thought to prevent coke deposition through the Boudouard reaction or to shift the equilibrium limitation by the removal of hydrogen as a water.

In this study, we report the oxidation capability of carbon dioxide in the dehydrogenation of ethylbenzene over V/MgO catalyst. The catalyst characterization was performed with the aim of elucidating the role of carbon dioxide in this reaction.

The catalyst was prepared by impregnating MgO (Ube Materials Industries Ltd., MgO-100A=153 m^2/g and 2000A=7.8 m^2/g) with NH_4VO_3 dissolved in an aqueous solution of oxalic acid. The loading level of vanadium was 1.0 mmol on 1 g of MgO. After impregnation, the catalyst was dried and calcined in air at 600 °C for 4 h. The reaction was carried out with a fixed-bed flow-type quartz reactor operated at an atmospheric pressure. All products were analyzed by gas chromatography. The catalysts treated under different conditions were analyzed by X-band ESR spectroscopy measured at an ambient temperature (modulation: 0.5 mT; sweep width: 330 ± 100 mT; microwave power: 2 mW).

Table 1 shows the results of the catalytic activity in the dehydrogenation of ethylbenzene with various vanadium catalysts in the presence and absence of carbon dioxide. A bulk V_2O_5 catalyst exhibited a styrene yield of 13.9% in the presence of carbon dioxide, and 15.3% in the absence of carbon dioxide. The dehydrogenation activity did not depend on the atmosphere with this catalyst (entry 1). The loading of vanadium on MgO having a large surface area markedly increased the styrene yield to 53.8% in the presence of carbon dioxide and 21.9% under an inert gas (argon) atmosphere (entry 2). The styrene yield in the presence of carbon dioxide was 2.5 times higher than that in argon atmosphere. During the reaction, carbon dioxide, corresponding to the amount of styrene produced, was reduced to carbon monoxide to give water. In contrast, the catalyst having a smaller surface area (different MgO source) exhibited only slight catalytic activity as compared to that with a large surface area. The promoting effect of carbon dioxide on the dehydrogenation of ethylbenzene was not observed with this catalyst (entry 3). In view of these findings, an adsorption site of carbon dioxide on the catalyst would be necessary for the promoting effect of carbon dioxide to be exhibited in the dehydrogenation of ethylbenzene.

In order to investigate the role of carbon dioxide in the dehydrogenation of ethylbenzene, the changes in the oxidation state of the vanadium species were characterized by ESR spectroscopy. Figure 1(a) shows the ESR spectrum of the fresh V/MgO-100A catalyst. The well-resolved hyperfine structures with eight parallel and perpendicular components were assigned to the V^{4+} ion.[9] On the other hand, the UV-visible spectra and X-ray diffraction of the fresh catalyst indicated that most of the

Table 1. Dehydrogenation of ethylbenzene with various vanadium catalysts [a]

Entry	Catalyst	Surface area	Under CO_2 flow			Under Ar flow			Y_{CO_2}/Y_{Ar} [b]
			EB Conv.	ST yield	ST selec.	EB Conv.	ST yield	ST selec.	
		m^2/g		%			%		%/%
1	V_2O_5	trace	21.5	13.9	64.7	21.8	15.3	70.2	0.91
2	V/MgO-100A	144	59.1	53.8	91.1	22.7	21.9	96.5	2.46
3	V/MgO-2000A	9	19.7	18.5	94.1	19.8	19.5	98.8	0.95

[a]Catalyst: 100 mg, vanadium: 1.0 mmol/g-MgO, reaction time: 1 h, W/F: 70 g-cat·h/mol, CO_2(Ar): 30 ml/min, reaction temperature: 550 °C. [b]Styrene yield (CO_2 flow) / styrene yield (Ar flow).

vanadium species were tetrahedral V^{5+} and $Mg_3V_2O_8$ (diamagnetic), respectively. It is supposed that a slight anion vacancy existed in the $Mg_3V_2O_8$ structure and that V^{4+} ions were highly dispersed in the V^{5+} ions.

The ESR spectrum of the catalyst after the dehydrogenation reaction with ethylbenzene in the presence of carbon dioxide (Figure 1(b)) was similar to that of the fresh catalyst, although the signal intensities decreased and another six-line appeared due to Mn^{2+} contained within MgO as an impurity. In contrast, the ESR spectrum after the reaction in the absence of carbon dioxide showed new eight-lines with a smaller hyperfine coupling constant superimposed on the V^{4+} signals (Figure 1(c)). Sharma et al. reported that this eight-line spectrum was assigned to the V^{2+} ion in octahedral symmetry.[9] This result shows that the oxidation state of the vanadium species in the presence of carbon dioxide was kept higher than that in the absence of carbon dioxide.

In order to confirm the oxidation of the reduced vanadium species by carbon dioxide, two ESR spectra were measured as follows. Figure 1(d) shows the ESR spectrum of the catalyst reduced with hydrogen at 550 °C for 6 h. A sharp eight-line spectrum due probably to V^{2+} was observed for the reduced catalyst as well as the catalyst after the reaction with ethylbenzene in the absence of carbon dioxide (Figure 1(c)). These results indicate that the reduction of vanadium species proceeds during the reaction with ethylbenzene in the absence of carbon dioxide. Subsequently, the eight-line feature of the hydrogen-reduced catalyst disappeared after treatment with carbon dioxide at 550 °C for 6 h. During the reaction, carbon monoxide was produced. The ESR spectrum of the carbon dioxide-treated catalyst was similar to that of the fresh catalyst. However, it exhibited weaker resonance of the V^{4+} hyperfine structure, and the spectrum due to Mn^{2+} still remained (Figure 1(e)), indicating that carbon dioxide oxidizes the reduced vanadium species to a higher oxidation state, although the catalyst cannot completely return to the state of the fresh catalyst.

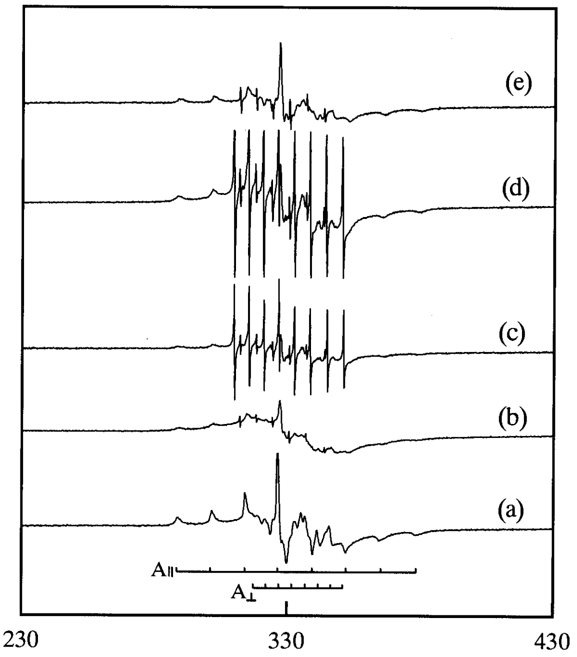
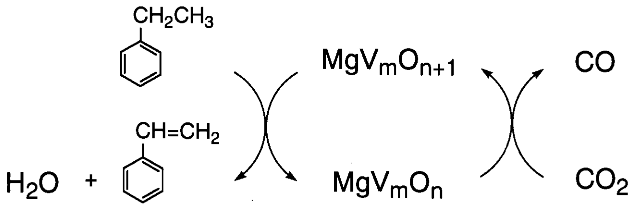


Figure 1. ESR spectra of V(1.0)/MgO-100A catalysts treated under various conditions.
(a) Fresh catalyst. (b) Dehydrogenated under CO_2 flow at 550 °C for 6 h. (c) Dehydrogenated under Ar flow at 550 °C for 6 h. (d) Fresh catalyst was reduced with H_2 at 550 °C for 6 h. (e) Treated with CO_2 at 550 °C for 6 h after the reduction with H_2.

To our knowledge, such an oxidation capability of carbon dioxide over vanadium oxide species has never been observed. According to thermochemical calculation (ΔG at 800-900 K), oxidation of lower valent vanadium oxides to V_2O_5 is highly difficult ($V^{4+} \rightarrow V^{5+}$; ΔG=156.5 kJ/atom O at 800 K). However, above findings strongly suggest that carbon dioxide can oxidize the lower valency state-vanadium species. During the dehydrogenation of ethylbenzene, vanadium species, V^{5+} is reduced to V^{4+} or much lower oxidation state; consequently, the catalytic activity of dehydrogenation decreased. Lower valency state vanadium species on MgO exhibited lower activity for the dehydrogenation of ethylbenzene, since the dehydrogenation of ethylbenzene did occur after the run 6 h in argon atmosphere. Under carbon dioxide atmosphere, however, the vanadium species is kept at a higher oxidation state (Scheme 1), thus the higher ethylbenzene conversion and styrene yield are achieved. The oxidation of lower valency state vanadium species with carbon dioxide could be assisted by the support magnesium oxide. Therefore, even if the bulk lower valency state vanadium oxides could not be oxidized to higher valency state with carbon dioxide, complex oxides of magnesium and vanadium or vanadium oxide on MgO could be oxidized to higher valency state with carbon dioxide.



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

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