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Promoting effect of carbon dioxide on the dehydrogenation of ethylbenzene over silica-supported vanadium catalysts

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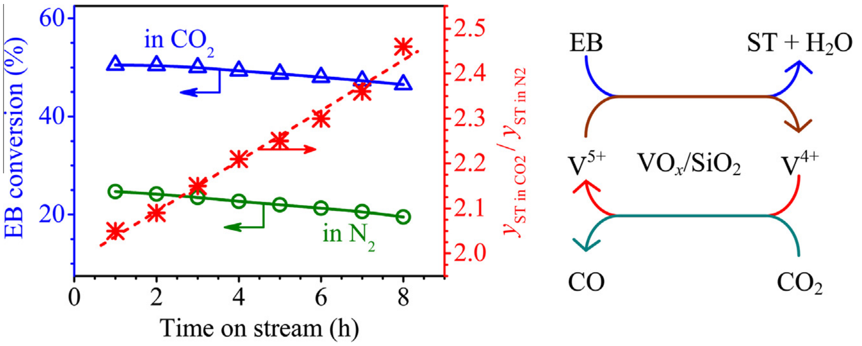
HIGHLIGHTS

- ▶ CO_2 has a prominent promoting effect on ethylbenzene (EB) dehydrogenation.
- ▶ EB dehydrogenation over VO_x/SiO_2 in CO_2 may follow a redox mechanism.
- ▶ CO_2 can effectively keep/regain high valence active vanadium species.
- ▶ CO_2 can alleviate catalyst deactivation, but cannot suppress coke formation.
- ▶ Coke quantity deposited is only related to the amount of EB converted.

GRAPHICAL ABSTRACT

For ethylbenzene (EB) dehydrogenation in CO_2 over VO_x/SiO_2 catalyst, a prominent promoting effect of CO_2 is observed. CO_2 can effectively keep/regain high valence vanadium species active for EB dehydrogenation.



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ABSTRACT

Dehydrogenation of ethylbenzene (EB) to styrene (ST) in the presence of carbon dioxide (CO_2) was carried out over silica-supported vanadium catalysts (VO_x/SiO_2) to investigate the role of CO_2 played in this reaction coupling process. A prominent promoting effect of CO_2 on EB dehydrogenation is observed; over VO_x/SiO_2 with a vanadium loading of 0.8 mmol/g-SiO_2, ST yield at 550 °C in CO_2 is 2.05 times higher than that in an inert atmosphere of nitrogen and the catalyst also deactivates much more slowly in CO_2. CO_2 as a soft oxidant can effectively keep/regain high valence vanadium species that are highly active for EB dehydrogenation, which is then conducive to enhancing EB conversion and suppressing catalyst deactivation. Both carbonaceous deposition and deep reduction of the active vanadium species contribute to the catalyst deactivation; however, CO_2 is only effective on alleviating the catalyst deactivation by protecting the high valance vanadium species from deep reduction, but is invalid in suppressing coke formation.

1. Introduction

Styrene (ST) is commercially produced in large scale by the dehydrogenation of ethylbenzene (EB) in the presence of a large quantity of superheated steam over a promoted iron oxide catalyst at 600–700 °C [1]. However, it is also a high energy-consuming process because much of the latent heat of steam is lost in the gas–liquid separator. Oxidative dehydrogenation is an effective way to increase the conversion and/or lower the reaction temperature; however, the desirable dehydrogenation product is vulnerable to deep oxidation when using oxygen as the oxidant [2,3]. Therefore, many researchers have attempted to employ carbon dioxide (CO_2) as a mild oxidant in the oxidative

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dehydrogenation of EB, where the dehydrogenation is coupled with reverse water gas shift (RWGS). The dehydrogenation of EB to ST in the presence of CO_2 instead of steam is believed to be an energy-saving and environmentally friendly process [4]. It is estimated that the energy required for producing ST in the new process using CO_2 is much lower than that needed in the current commercial process [5]. Moreover, as a gas contributing toward inducing the greenhouse effect, CO_2 used in this process is readily available, inexpensive and nontoxic.

Various catalysts containing Fe [5–11], Cr [12,13], and V [14–28] were found to be active for EB dehydrogenation in CO_2. Among these catalysts, the supported vanadium catalysts showed good performance in EB dehydrogenation. Sakurai et al. [15] found that vanadium oxide-loaded MgO catalyst exhibited high promoting effect of CO_2 on its catalytic activity, but suffered from severe deactivation even in several hours. We also reported that vanadium oxides supported on Al_2O_3 were more active and stable for the dehydrogenation of EB in CO_2 than in N_2 [18,19], though ST yield in CO_2 was only 1.12 times higher than that in N_2 at 550 °C. Li et al. [27] reported that vanadia supported on mesocellular silica foam exhibited high activity for EB dehydrogenation in CO_2 due to the improved reducibility and diffusion of reactants and products in the catalysts. Liu et al. [28] found that $V_2O_5/Ce_{0.6}Zr_{0.4}O_2$–$Al_2O_3$ was an efficient catalyst for EB dehydrogenation in CO_2 and proposed a redox mechanism involving oxidation–reduction recycling of Ce^{3+}/Ce^{4+} and V^{5+}/V^{4+} in a highly dispersed state. For EB dehydrogenation in CO_2, it was generally accepted that CO_2 may eliminate hydrogen produced from the dehydrogenation through RWGS and alleviate the catalyst deactivation by partially removing the carbonaceous deposition and keeping the active phase during the reaction [7,19].

Extensive researches have been made to improve the catalyst activity and stability for EB dehydrogenation in the absence of steam [4–28], in the meanwhile, however, there were still a lot of controversies on understanding the reaction mechanisms and the role of CO_2 played in EB dehydrogenation. Silica (SiO_2) is generally chemically inert and neutral in acidity, a simple catalyst like silica-supported vanadium (VO_x/SiO_2) is proper to bring the interaction between CO_2 and catalytically active species as well as the promoting effect of CO_2 on EB dehydrogenation coupled with RWGS into prominence. Therefore, in this work, EB dehydrogenation in CO_2 was carried out over VO_x/SiO_2 to investigate the role of CO_2 played in this reaction coupling process.

2. Experimental

2.1. Catalyst preparation

SiO_2 powder (obtained from Zhoushan Nanometer Materials Co. of China) with a BET surface area of 175 m^2/g, a pore volume of 0.57 cm^3/g, and a granularity of 20–40 nm was used as the catalyst supports; it was activated at 550 °C in air for 2 h before use. VO_x/SiO_2 catalysts were prepared through the incipient wetness impregnation of SiO_2 with NH_4VO_3 dissolved in an aqueous solution of oxalic acid. The impregnation lasted for 24 h, and then the catalysts were dried at 120 °C in air for 4 h and further calcined at 550 °C in air for 4 h.

2.2. Catalyst characterization

BET surface area of the catalysts was measured by nitrogen (N_2) adsorption at −195.7 °C with a physisorption analyzer (ASAP2000, Micromeritics Instrument Co., USA). The samples were degassed at 200 °C and 6.7 Pa for 2 h prior to the measurement.

X-ray powder diffraction (XRD) patterns of the catalysts were collected on a powder X-ray diffractometer (Shimadzu 6100) with a monochromated Cu $K\alpha$ (40 kV/30 mA) radiation source. The measurements were made from 10° to 70° with a scanning rate of 4°/min.

Diffuse reflectance UV–Visible (DR UV–Vis) spectra of the catalysts were recorded on a UV-2501 PC (Shimadzu) spectrophotometer. The spectra were collected in the wave length of 200–800 nm at room temperature.

Temperature programmed reduction by hydrogen (H_2-TPR) was performed in a quartz micro reactor TP-5000 (Tianjin-Xianquan, China) connected with a mass spectroscopy (Omni Star 200); about 50 mg catalyst sample was used in each measurement. The catalyst sample was first pretreated in air at 300 °C for 1 h, followed by purging with N_2 at the same temperature for 1 h and then cooling down to room temperature. After that, the flow of 7% H_2 diluted in N_2 (50 ml/min) was switched into the system, and the sample was then heated up from room temperature to 800 °C at a ramp of 10 °C/min. The amount of hydrogen uptake during the heating for reduction was measured by a thermal conductivity detector (TCD).

Thermogravimetric analyses (TGA) were carried out on a thermal balance (TGA92, Setaram Co., France) under air within the temperature range of 20–600 °C at a heating rate of 10 °C/min. Coke quantity deposited in the used catalysts after reaction were determined by the weight loss of catalyst sample during the heating process.

2.3. Catalyst tests and analytic procedures

Catalytic reaction was carried out in a stainless steel tube reactor with an inner diameter of 6.0 mm. The catalyst (100–500 mg) was placed at the center of the reactor using quartz glass wool as plugs. All the reaction tests were performed under atmospheric pressure (0.1 MPa) and 550 °C, since previous works proved that such a condition is quite appropriate to get a content conversion of EB and selectivity to ST for EB dehydrogenation in CO_2 [7,18,19,29]. Before each test, the catalyst was first activated under a nitrogen flow from room temperature to the reaction temperature, and then the nitrogen flow was switched to CO_2. The catalyst was maintained at this temperature in CO_2 for 15 min before introducing EB (1.63 mmol/h) by a micro feeder pump. The effluents, including ST, unreacted EB, and by-products like benzene and toluene, were condensed in a trap with an ice water bath.

The liquid products were analyzed with an FID gas chromatograph (Shimadzu GC-7A) equipped with a 3 mm × 3 m stainless-steel column packed with OV-101. The gaseous products (CO_2, CO, H_2 and CH_4) were analyzed by a TCD gas chromatograph (Shimadzu GC-9A) equipped with a 3 mm × 3 m stainless-steel column packed with carbon molecular sieves.

3. Results and discussion

3.1. Promoting effect of CO_2 on EB dehydrogenation

EB dehydrogenation in CO_2 is compared with that in inert N_2 over VO_x/SiO_2 with different vanadium loadings, as shown in Table 1. Pure SiO_2 support and bulk V_2O_5 exhibit poor activity for EB dehydrogenation in both atmospheres. By loading vanadium on SiO_2, the VO_x/SiO_2 catalysts exhibit high activity for EB dehydrogenation, especially in CO_2. The vanadium species are isolated or highly dispersed in the catalyst with a low vanadium loading; with the increase of vanadium loading, although more surface vanadia species are produced, the polymerization of vanadium species is also intensified, which forms less catalytically active crystal vana-