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Ethylbenzene dehydrogenation in the presence of carbon dioxide over alumina supported catalysts

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Abstract

The dehydrogenation of ethylbenzene to styrene was performed in the presence of carbon dioxide instead of steam over a series of alumina supported catalysts, which was believed to be an energy-saving and environmentally friendly process. The effects of active components, promoters, textural properties and other preparation parameters on the catalyst behaviors were examined. The results indicated that the conversion of ethylbenzene could be greatly improved by the reaction coupling due to the simultaneous elimination of hydrogen produced from the dehydrogenation, and vanadium supported on alumina with chromium as promoter was suggested to be promising catalysts. With the catalyst VCr/Al_2O_3, high ethylbenzene conversion (about 50%) and selectivity to styrene (95–99%) at lower temperature (550 °C) was achieved with reasonable stability (>70 h). The main cause of catalyst deactivation is the coke deposition, which may be alleviated in the presence of carbon dioxide. The catalytic activity of V/Al_2O_3 can be resumed completely after burning the coke by air or diluted air. Moreover, the catalyst characterization showed that high ratio of mesopore in the γ-Al_2O_3 support could benefit the catalyst activity and stability.

Keywords: Reaction coupling; Ethylbenzene dehydrogenation; Styrene; Water-gas shift; Carbon dioxide; V/Al_2O_3 catalysts

1. Introduction

Styrene (ST) is commercially produced by the dehydrogenation of ethylbenzene (EB) on the promoted iron oxide catalysts at 600–700 °C, just below the temperature where thermal cracking becomes significant. Because this reaction is highly endothermic and volume-expanding, a large amount of superheated steam is used to supply heat, lower the partial pressure of the reactant, and avoid the deposition of carbonaceous substance. However, much of the latent heat of steam is lost in the gas–liquid separator without recovery [1]. Thus, it is highly desirable to search for the alternative technologies such as oxidative dehydrogenation and reaction coupling, which can lower the reaction temperature and water/EB ratio, and then the energy consumption.

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 [2–5]. Since the commercial Fe–Cr–K catalysts do not work effectively in such coupling system, the catalysts have been screened extensively and some new catalysts were reported [1,3–17]. Inorganic oxides (Al_2O_3, MgO, ZnO, WO_3, SiO_2 and ZrO_2), various zeolites, as well as a wide range of carbonaceous materials such as activated carbon (AC) were used as the supports. Various metals (Fe, V, Cr, Cu, Zr, Ce, La, Na, Ni and Co) were adopted as the active components, and the alkaline metals (Li, Na and K), alkali earth metals (Ca and Mg) and other elements (Sb and Cr) were introduced as the promoters.

Among these works, Mimura et al. [4,5,8] found that 10 wt.% Fe_2O_3/Al_2O_3 prepared by coprecipitation was effective for EB dehydrogenation in the presence of CO_2, and the addition of proper amount of CaO to Fe/Al_2O_3 based catalysts could suppress the deactivation. Park et al. [12] found that ZrO_2 was active for EB dehydrogenation at 600 °C, especially in the presence of CO_2; the catalytic activity was associated with the surface area and basicity that related to CO_2 affinity. Badstube et al. [9] investigated the catalytic behavior of iron supported on AC in the EB dehydrogenation coupled with the reverse water-gas shift (RWGS), and observed high EB conversion and selectivity to ST at 550 °C. Sakurai et al. [11] investigated the dehydrogenation of EB over carbon-supported vanadium catalysts at 450–650 °C; the conversion in the presence of CO_2 was 14.0% higher than that in the presence of argon. Sugino et al. [7] and we [13] also found that the activated

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carbon-supported iron and vanadium oxides promoted by alkali metal oxides behaved well for the EB dehydrogenation in the presence of CO_2. The carbonaceous supported catalysts showed better initial activity, while the alumina supported catalyst maintained longer stability.

However, the EB conversion observed in such coupling system is still much lower than the equilibrium conversion [2,3]; the results in the references were mostly obtained at low EB space velocity and high CO_2/EB ratio, which was far from any practical use; the current catalysts have a series of problems such as deactivation; and the intrinsic factors of such reaction coupling still have a lot of controversies until now. Therefore, considerable work is still necessary on exploring the mechanism of reaction coupling, optimizing the coupling process and screening for better catalysts with both reasonable activity and stability.

In this work, EB dehydrogenation to ST was performed in the presence of CO_2 over catalysts V, Fe, Cu and Pt supported on γ-Al_2O_3; the effects of the active components, promoters, and preparation and reaction conditions upon the ST yield and catalyst stability were examined. It was revealed that the EB conversion could be greatly improved by the reaction coupling due to the simultaneous elimination of the hydrogen produced from the dehydrogenation. V/Al_2O_3 promoted by Cr showed reasonable stability and activity. Textural characterization and temperature-programmed oxidation (TPO) indicated that the coke deposition was the main reason for catalyst deactivation, and the deactivated catalyst can be easily regenerated by decoking with air.

2. Experimental

2.1. Catalyst preparation

All the catalysts in this work were prepared by impregnation or co-impregnation method. γ-Al_2O_3 (obtained from Institute of Coal Chemistry, Chinese Academy of Sciences) with a BET area of 275 m^2/g, a pore volume of 0.70 cm^3/g and an average pore aperture of 10 nm was used as the catalyst support, which was first crashed and sieved to 20–40 mesh, and then activated at 500 °C for 2 h before use. The active components Fe, Cu, Pt, V were introduced by the impregnation of supports with aqueous solutions of iron nitrate, copper nitrate, chloroplatinic acid and NH_4VO_3 with oxalic acid, respectively. Alkali metal (Li, K), alkaline earth metal (Ca), transition metal (Mn, Cr, Zr) and rare earth metal (La) promoted catalysts were prepared by co-impregnation of a solution containing both the active components and nitrates of the promoters. The impregnation lasted for 18 h, and then the catalysts were dried at 120 °C in air for 4 h. Then the catalysts Pt/Al_2O_3, Cu/Al_2O_3 and V/Al_2O_3 were calcined at 500–600 °C in air for 4 h, while Fe/Al_2O_3 at 650 °C for 5 h. The combined catalyst Fe–V/Al_2O_3 was prepared by the multiple-step impregnation: the Al_2O_3 support was first impregnated with iron nitrate solution followed by calcination at 650 °C in air for 5 h; and then the Fe/Al_2O_3 obtained was impregnated with NH_4VO_3 dissolved in an aqueous solution of oxalic acid, followed by calcination at 550 °C in air for 4 h. Impregnation in this order is due to the fact that the calcination temperature for Fe/Al_2O_3 was higher than that for V/Al_2O_3, and such a consideration was also helpful to avoid V-loss during the catalyst preparation.

2.2. Reaction and analytical procedures

The catalytic reaction was performed in a stainless steel tube reactor with an inner diameter of 6.0 mm, and about 200 mg catalyst was used per run. Before the reaction, the catalyst was first activated under a nitrogen flow from the room temperature to reaction temperature, and then the nitrogen flow was switched to CO_2. The catalyst was maintained at this temperature in a CO_2 stream for 10 min before introducing EB (20.4 mmol EB/g_{cat} h) by a micro feeder pump. The molar ratio of CO_2 to EB was fixed at 11. The reaction was operated at 550 °C or 600 °C at atmospheric pressure. The effluents, including ST, benzene, toluene, and unreacted EB from the reactor were condensed in a trap by 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 of OV-101. The gaseous products (H_2, N_2, CO, CO_2, CH_4, and C_2H_6) were analyzed by a TCD gas chromatograph (Shimadzu GC-9A) equipped with a 3 mm × 3 m stainless-steel column of carbon molecular sieve.

2.3. Catalyst regeneration

The catalyst regeneration was carried out in the presence of air, diluted air (25%) or CO_2 atmosphere in the same reactor as that for the EB dehydrogenation. The deactivated catalyst after reaction was firstly flushed with nitrogen at high space velocity to remove any remains of reactants or products in the reactor; and then the nitrogen flow was switched to the regeneration atmosphere after the temperature in the catalyst bed reached the decoking temperature. The regeneration by air or diluted air were conducted at 500 °C with a space velocity of 10 000 h^{-1} for 1 h, while the regeneration by CO_2 was carried out at 550 °C with the same CO_2 flow as that in the coupling reaction for 4–12 h.

2.4. Catalyst characterization

Surface area and textural properties of the catalysts were measured by nitrogen adsorption at 77.4 K with ASAP2000 (Micromeritics Instrument Co., USA). The catalysts were degassed at 200 °C and 6.7 Pa for 4–5 h prior to the measurement.

The characteristics of the coke depositions were determined by TPO with a thermogravimetric analysis instrument (TGA92) connected to a mass spectroscopy (Omni Star 200). The mixed gas of O_2(5%)/Ar was introduced at a flow rate of 40 ml/min. The chamber filled with 20 mg catalyst sample was heated up from room temperature to 800 °C at a heating rate of 10 °C/min, and the sample weight and the amounts of CO_2 and water released during the heating-up were recorded simultaneously.

3. Results and discussion

3.1. Screening of active components

The catalytic behaviors of Fe, V, Pt and Cu supported on γ-Al_2O_3 for EB dehydrogenation in the presence of CO_2 were investigated at 550 °C. As showed in Fig. 1, Fe and V showed much better activity than Pt and Cu, although all the catalysts gave high selectivity to ST. The ST yield over Pt and Cu increased slowly with the time on stream. The ST yield over both Fe and V showed a decrease tendency, but the activity of V catalyst decreased much more slowly than that of Fe catalyst with the time on stream. Vanadium supported on γ-Al_2O_3 showed the best catalytic behavior among the catalysts investigated, with the ST yield of initial about 45% and still higher than 40% after 30 h on stream.

3.2. Influence of vanadium loading and calcination temperature

Figs. 2 and 3 showed the influence of vanadium loading and calcination temperature respectively on the catalytic behavior of vanadium supported on γ-Al_2O_3 for the EB dehydrogenation in the presence of CO_2 at 550 °C. It can be seen that the activity of V/Al_2O_3 increased with the vanadium loading at low loadings, and reached a high level at loading of 0.57–0.86 mmol/$g_{support}$. The stability of V/Al_2O_3 became worse at higher vanadium loading (>1.15 mmol/$g_{support}$). The results of several catalysts calcined at different temperatures (see Fig. 3) proved that calcination at 550 °C was favorable for the improvement of selectivity and activity of V/Al_2O_3. Therefore, V/Al_2O_3 with a vanadium loading of 0.57 mmol/$g_{support}$ and calcined at 550 °C for 4 h was preferred for the EB dehydrogenation in the presence of CO_2.

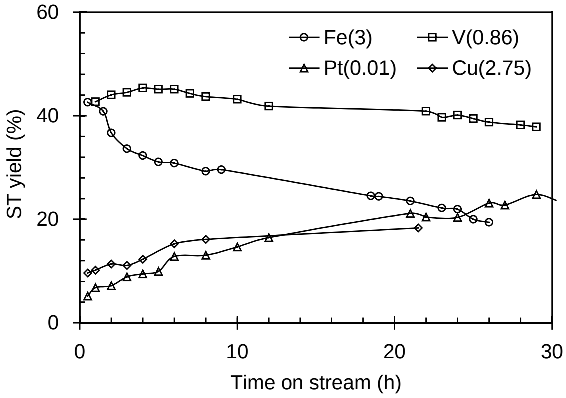

Fig. 1. Catalytic behaviors of alumina supported catalysts with various active components: the ST yield with the time on stream (550 °C, $W/F = 4.07\ g_{cat}$ h/mol, CO_2/EB = 11, and the numerals in the legend indicate the amounts of metal species in mmol/$g_{support}$).

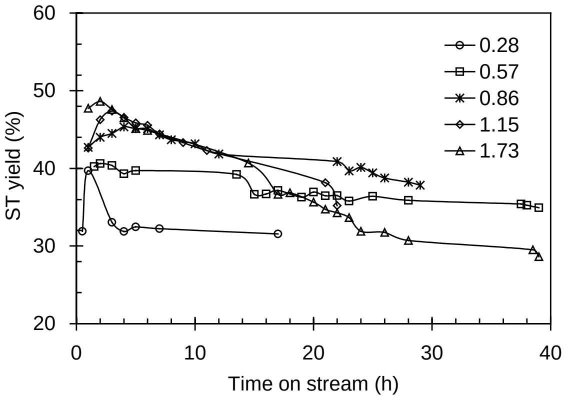

Fig. 2. Influence of vanadium loading (the numerals in the legend, in mmol/$g_{support}$) on the activity of V/Al_2O_3 catalysts: the ST yield with the time on stream (550 °C, $W/F = 4.07\ g_{cat}$ h/mol, CO_2/EB = 11).

3.3. Effects of promoters

In order to improve the activity and selectivity of Fe, V supported on γ-Al_2O_3, the effects of various promoters were investigated. As shown in Fig. 4, the catalytic activity of Fe/Al_2O_3 can be promoted by the addition of Ca, Mn and Cr, and the highest initial ST yield of about 48% was achieved over the Cr-promoted Fe(3)Cr(0.3)/Al_2O_3. When mixed with vanadium, the activity of Fe/Al_2O_3 can be further improved.

Fig. 5 showed the catalytic behaviors of V/Al_2O_3 catalysts modified by various promoters. The addition of Li, K, Mg, Mn, Co and Zr had little influence on the catalytic activity, while the addition of La (0.3 mmol/$g_{support}$) could even lead to a decrease in the catalytic activity. Among the promoters

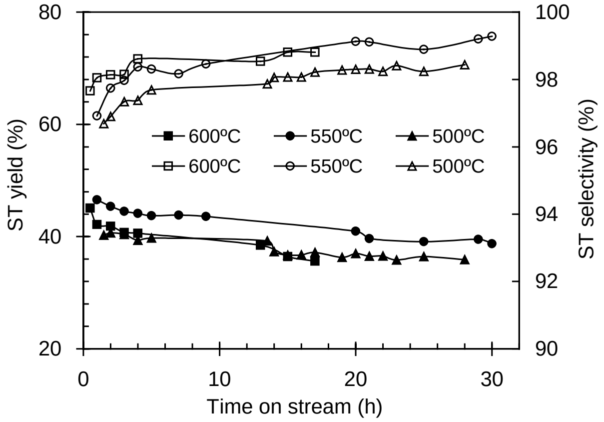

Fig. 3. Influence of calcinations temperature (4 h duration) on the activity of V(0.57)/Al_2O_3 catalysts: the ST yield (closed symbols) and selectivity (open symbols) with the time on stream (550 °C, $W/F = 4.07\ g_{cat}$ h/mol, CO_2/EB = 11).

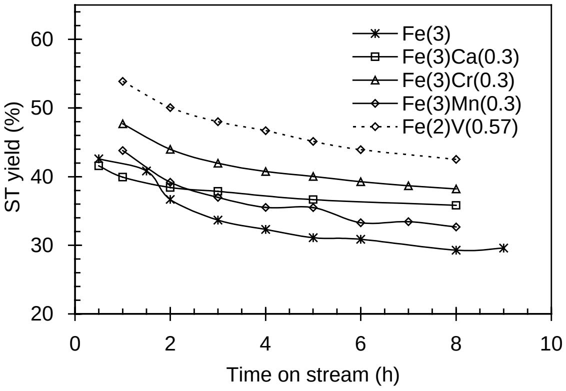

Fig. 4. Catalytic behaviors of Fe(3)/Al_2O_3 modified with various promoters: the ST yield with the time on stream (550 °C, $W/F = 4.07\,g_{cat}$ h/mol, CO_2/EB = 11, and the numerals in the legend indicate the amounts of metal species in mmol/$g_{support}$).

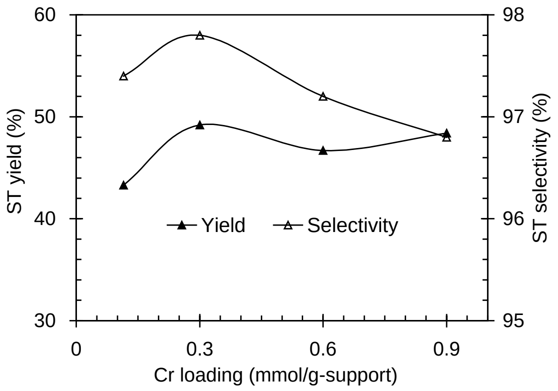

Fig. 6. Influence of Cr loading on the activity of V(0.57)Cr/Al_2O_3 catalysts: the ST yield (closed symbols) and selectivity (open symbols) with the Cr loading (550 °C, $W/F = 4.07\,g_{cat}$ h/mol, CO_2/EB = 11, data were acquired after reaction lasted for 3 h).

investigated, only Cr showed an evidently positive effect on the ST yield, which increased from 45% over V(0.57)/Al_2O_3 to 50% over V(0.57)Cr(0.3)/Al_2O_3. This may be due to that Cr is not only an active component for the dehydrogenation, but also an effective promoter to the RWGS.

The effect of Cr loading on the activity of VCr/Al_2O_3 catalyst was also investigated. As shown in Fig. 6, at low Cr loading, the activity of VCr/Al_2O_3 catalyst increased with the loading; when the Cr loading exceeded 0.3 mmol/$g_{support}$, the ST yield over VCr/Al_2O_3 kept at a flat level, while the ST selectivity decreased gradually.

3.4. *Effects of reaction coupling*

In order to elucidate the superiority of reaction coupling over dehydrogenation only with the dilution by the inert gas, the dehydrogenation of EB was also carried out in the presence of nitrogen over V/Al_2O_3, VCr/Al_2O_3, Fe/Al_2O_3 and FeCr/Al_2O_3 at 550 °C (see Table 1). Just as suggested by the thermodynamic analysis [2,3], EB conversion can be improved greatly by the reaction coupling with the RWGS over V/Al_2O_3 and VCr/Al_2O_3. As shown in Fig. 7, the ST yield in the presence of CO_2 was always higher than that in the presence of nitrogen within 30 h on stream, which proved the superiority of the reaction coupling.

However, the enhancement of EB conversion in the presence of CO_2 other than nitrogen was not observed on Fe/Al_2O_3 and FeCr/Al_2O_3 catalysts. This phenomenon was also described by Mimura et al. [4]; the initial ST yield on Fe/Al_2O_3 catalyst in the presence of CO_2 was lower than that in the presence of helium, but the catalyst stability is much better in the presence of CO_2. Recently, Saito et al. [18] found that the ST yield in the presence of CO_2 was lower than that in the presence of helium at short contact time (*W/F*); while at longer contact time, the sequence was reversed. The reason may be that the elimination of hydrogen produced by the dehydrogenation is limited, and the coupled reactions are far from the equilibrium under current reaction conditions.

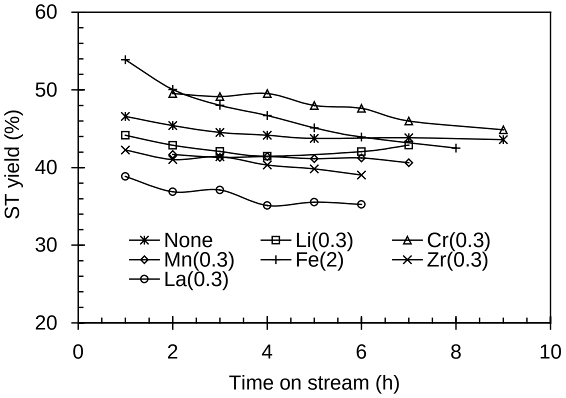

Fig. 5. Catalytic behaviors of V(0.57)/Al_2O_3 catalysts modified by various promoters: the ST yield with the time on stream (550 °C, $W/F = 4.07\,g_{cat}$ h/mol, CO_2/EB = 11, and the numerals in the legend indicate the amounts of metal species in mmol/$g_{support}$).

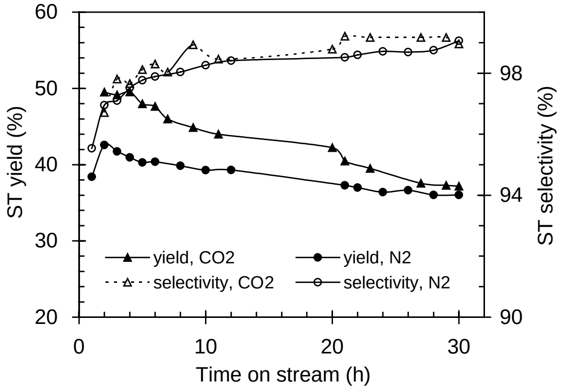

Fig. 7. Catalytic behaviors of V(0.57)Cr(0.3)/Al_2O_3 in the presence of different gases: the ST yield (closed symbols) and selectivity (open symbols) with the time on stream (550 °C, $W/F = 4.07\,g_{cat}$ h/mol, CO_2 (or N_2)/EB = 11).

Table 1
EB dehydrogenation in the presence of CO_2 or nitrogen over Fe, V supported on γ-Al_2O_3 catalysts[a]

Active components[b]	CO_2		N_2	
	EB conversion (%)	ST selectivity (%)	EB conversion (%)	ST selectivity (%)
V(0.57)	45.5	97.8	37.4	98.1
V(0.57)Cr(0.3)	50.3	97.8	43.0	97.0
Fe(3)	35.0	96.3	34.2	96.2
Fe(3)Cr(0.3)	42.9	97.9	43.6	97.9

[a] Reactions were performed at 550 °C and atmospheric pressure ($W/F = 4.07\,g_{cat}$ h/mol, CO_2 (or N_2)/EB = 11). Data was acquired after reaction lasted for 3 h.

[b] Numerals in parentheses indicate amounts of metal species in mmol/$g_{support}$.

3.5. Catalysts deactivation and regeneration

One of the major problems in the new EB dehydrogenation process is the deactivation of catalyst. In our previous work [13], it was shown that the activated carbon-supported catalysts with high initial yield of ST at 550 °C deactivated rapidly in the first 6 h and then slowly with the time on stream, and the catalyst activity could be resumed to some extent after regeneration by CO_2. However, the γ-Al_2O_3 supported catalysts, especially V/Al_2O_3, showed much better stability. As shown in Fig. 8, the ST yield in this work decreased only from initial 40% to 30% after 70 h on stream, while the catalyst stability with a lifetime more than 25 h for the EB dehydrogenation in the presence of CO_2 had not yet been reported.

In order to find out the causes of catalyst deactivation and to determine the regeneration conditions, V/Al_2O_3 deactivated after 30 h on stream was characterized by TPO. As shown in Fig. 9, there was only one decoking peak at about 510 °C. Another peak for water at 165 °C was due to the releasing of water adsorbed on γ-Al_2O_3.

After the regeneration by air or diluted air, the catalytic activity of V(0.57)/Al_2O_3, which was deactivated to some extent after 70 h on stream, was completely resumed (see Fig. 8). This indicates that the coke deposition on the surface is the main cause for the catalyst deactivation. After burning the coke deposited, the catalytic activity can be completely resumed; and furthermore, the lifetime of the regenerated V/Al_2O_3 could even be prolonged to some extent. The ST yield over the regenerated V/Al_2O_3 catalyst decreased from the initial 40–30% only after 100 h on stream.

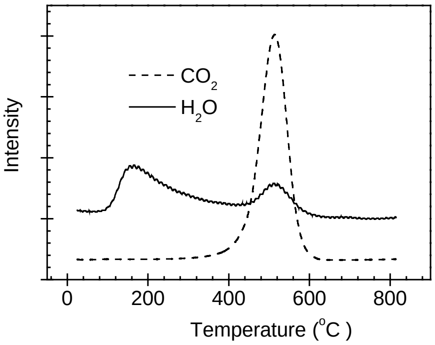

Fig. 9. TPO of V(0.57)/Al_2O_3 deactivated after 30 h on stream: the releasing intensities of CO_2 and water with the temperature at a heating rate of 10 °C/min.

The regeneration of catalysts by CO_2 was also investigated to elucidate its role in the reaction coupling. The regeneration of V/Al_2O_3 after 30 h on stream was carried out at reaction temperature (550 °C), in the presence of equal amount of CO_2 to that of the dehydrogenation process. As shown in Fig. 10, the initial activity was mostly resumed

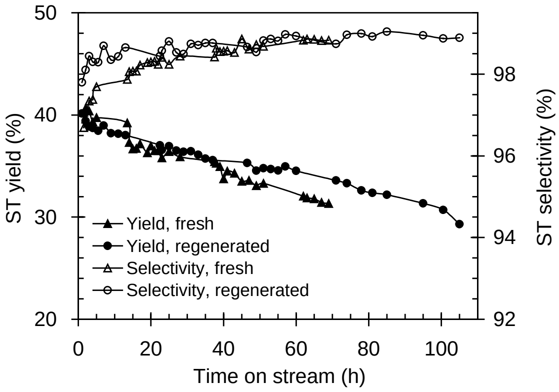

Fig. 8. Catalytic behaviors of fresh and air regenerated V(0.57)/Al_2O_3 for the EB dehydrogenation in the presence of CO_2: the ST yield (closed symbols) and selectivity (open symbols) with the time on stream (550 °C, $W/F = 4.07\,g_{cat}$ h/mol, CO_2/EB = 11).

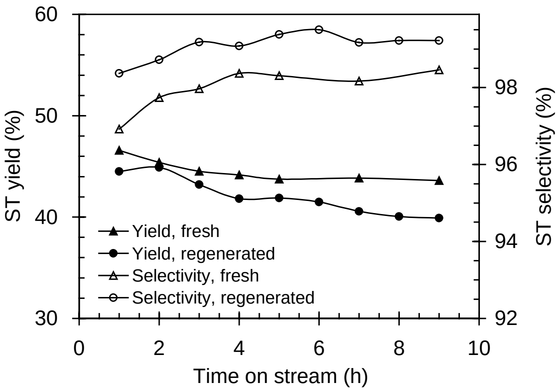

Fig. 10. Catalytic behaviors of fresh and CO_2 regenerated V(0.57)/Al_2O_3 catalysts for the EB dehydrogenation in the presence of CO_2: the ST yield (closed symbols) and selectivity (open symbols) with the time on stream (550 °C, $W/F = 4.07\,g_{cat}$ h/mol, CO_2/EB = 11).

Table 2
BET surface and textural characterization of vanadium catalysts supported on alumina

Active components[a]	ST yield[b] (%)	Surface area (m^2/g)	Micropore area (m^2/g)	Average pore size (nm)	Total pore volume (cm^3/g)
None[c]	–	275	5.4	10.2	0.70
V(0.57)[c]	46.6	245	6.6	10.0	0.64
V(0.57) (30 h)[d]	–	193	0	8.7	0.42
V(0.57) (30 h, reg., air)[e]	45.7	219	22.5	10.3	0.56
V(0.57) (30 h, reg., CO_2)[f]	44.5	195	2.2	9.3	0.46
V(0.58)Cr(0.3)[c]	49.2	256	12.2	9.8	0.63
V(0.57)Cr(0.3) (30 h)[d]	–	173	0	8.4	0.38
V(0.57)Cr(0.3) (8 h, reg., air)[g]	–	245	16.7	10.3	0.63
V(0.57)Cr(0.3) (8 h, reg., CO_2)[h]	–	213	19.5	10.0	0.55

[a] Numerals in parentheses indicate the amounts of metal species in mmol/$g_{support}$.

[b] Reactions were performed at 550 °C and atmospheric pressure ($W/F = 4.07\, g_{cat}$ h/mol, CO_2/EB = 11), and the ST yield was acquired after reaction lasted for 1 h.

[c] Fresh catalysts.

[d] Used catalysts after 30 h on stream for EB dehydrogenation in the presence of CO_2.

[e] Catalysts, which was first used after 30 h on stream, then regenerated by air or diluted air.

[f] Catalysts, which was first used after 30 h on stream, then regenerated by CO_2 for 12 h.

[g] Catalysts, which was first used after 8 h on stream, and then regenerated by air or diluted air.

[h] Catalysts, which was first used after 8 h on stream, then regenerated by CO_2 for 12 h.

after decoking by CO_2 for 12 h. After decoking by CO_2, the activity of different catalysts was mostly or at least partly resumed, indicating that CO_2 could alleviate the catalyst deactivation during the reaction course.

3.6. *BET surface and textural characterization*

In order to elucidate the mechanism of catalyst deactivation, the surface areas and textural properties of γ-Al_2O_3 supported vanadium catalysts, fresh, deactivated and regenerated by air and CO_2, were then examined (see Table 2). For the fresh V/Al_2O_3 catalyst, the addition of promoter Cr led to a little increase in the surface area; after 30 h on stream, 21% of surface area was lost over V/Al_2O_3 catalyst and 32% was lost over VCr/Al_2O_3 catalyst. The decrease of catalysts surface area and pore volume resulted from the disappearance of micropores and even the reduction in mesopore size, which can be seen from the decrease of the average pore size. However, the coke deposition to such degree had limited effect on the activity of V/Al_2O_3; the ST yield loss was only 10% after 70 h on stream for the EB dehydrogenation in the presence of CO_2.

The ratio of mesopores in active carbon was about 51%, while that in γ-Al_2O_3 was nearly 100%, which suggested that the enhancement in the mesopore ratio was in favor of the stability of the catalysts. Moreover, after regeneration by air or diluted air, the surface area and pore volume of V/Al_2O_3 were resumed fairly well; while after regeneration by CO_2 decoking, a partial resumption in surface area and pore volume was observed. The introduction of Cr seemed to be able to promote the regeneration process. The variation of surface area and pore volume was associated with the catalytic behaviors.

4. Conclusions

The dehydrogenation of EB was carried out in the presence of CO_2 over catalysts of iron, vanadium, platinum and copper supported on γ-Al_2O_3. It was revealed that the conversion of EB could be greatly improved by the reaction coupling due to the simultaneous elimination of the hydrogen produced from the dehydrogenation. The active components, promoters, and calcinations temperature had apparent influences on the activity of V/Al_2O_3 and Fe/Al_2O_3 catalysts. Vanadium oxide supported on γ-Al_2O_3 was suggested to be a promising catalyst for EB dehydrogenation in the presence of CO_2 with reasonable stability and activity. With the addition of Cr promoter, EB conversion of 50–60% and selectivity to ST of 95–99% were observed at 550 °C with a lifetime longer than 70 h.

Coke deposition on the surface resulting in the disappearance of micropore and reduce of mesopore was the main cause of the catalyst deactivation. After regeneration by air or diluted air, the catalytic activity of V/Al_2O_3 catalyst can be resumed completely. After regeneration by carbon oxide decoking, the activity was mostly or at least partly resumed, indicating that carbon oxide could alleviate the coke deposition on the catalysts during reaction. Moreover, the catalyst characterization showed that high ratio of mesopore in the γ-Al_2O_3 could benefit the catalyst activity and stability.

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