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Supported vanadia catalysts for dehydrogenation of ethylbenzene with CO_2

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Alumina supported vanadia catalysts (V/Al) for selective oxidehydrogenation of ethylbenzene with CO_2 were prepared by impregnation method. During preparation the effect of promoters and calcined temperature was investigated, it was found these two items had a strong influence on the activity of V/Al catalysts. Dehydrogenation reaction with CO_2 was happened in the fixed-bed reactor at 450 °C. Results showed that 15.2% ethylbenzene conversion and 99.2% styrene selectivity were acquired when V_2K/Al catalyst was used.

KEY WORDS: dehydrogenation; ethylbenzene; styrene; carbon dioxide; supported catalyst.

1. Introduction

At present, the commercial process of the dehydrogenation of ethylbenzene (EBDH) to styrene (ST) is widely running over iron oxide catalysts at 873–973 K, which is thermodynamically limited and, moreover, it is a very energy consuming process because of the required excess of superheated steam [1–3]. Thus, it is highly desirable to develop new process and catalysts that can decrease the reaction temperature.

The EBDH process was improved in the ways of common oxidation, oxidative dehydrogenation of ethylbenzene, dehydrogenation of ethylbenzene-selective-oxidation of hydrogen. However, none of these processes has been commercially produced so far. Recent years, carbon dioxide being used as a soft oxidant in the selective catalytic oxidehydrogenation of hydrocarbons has been extensively involved in. The EBDH with CO_2 (CO_2–EBDH) process could be effective in respect of utilization of CO_2 resource, being energy saving and environmentally friendly [4,5]. Since Fe–K-based catalysts used for present commercial dehydrogenation process do not work effectively in the presence of CO_2, a high performance catalyst for EBDH in the presence of CO_2 need be further developed.

Some researchers have reported their catalysts for the CO_2–EBDH. Suzaki and co-workers [6,7] reported that active carbon-supported vanadium catalysts exhibit high catalytic activity, afforded high styrene yield at 550 °C in EBDH to styrene in the presence of carbon dioxide. However, it suffered from severe catalyst deactivation due to coke deposition. 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. The reduced species, V^{4+} and V^{3+}, were less reactive sites for the dehydrogenation. Vislovskiy *et al.* [8] investigated the dehydrogenation of ethylbenzene to styrene with carbon dioxide using various vanadia–alumina catalysts, found that redox behavior of vanadium oxide played a key role in the dehydrogenation, revealing that the addition of the antimony oxide leads to the easier redox cycle between fully oxidized and reduced vanadium species. Sun *et al.* [9] examined the performances of various Fe and V supported catalysts on the EBDH in the presence/absence of CO_2 under 550 °C and investigated the role of CO_2 by means of TPD.

In this paper, we further investigated the effect of the promoter and the calcined temperature on the CO_2–EBDH reaction and the stability of the catalyst, the aim of this work was to find a better catalyst for the CO_2–EBDH process at a lower reaction temperature (≤450 °C) with a higher selectivity to styrene and higher ethylbenzene conversion.

2. Experimental

2.1. Catalyst preparation

The catalysts were prepared by an impregnation method, γ-Al_2O_3 with a specific surface area of 141.22 m^2/g was used as support. The active component V was introduced by aqueous solutions of metavanadate (NH_4VO_3) with oxalic acid. The impregnation lasted for 24 h with stirring and then the catalysts were dried at

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120 °C in air for 12 h. After that, the catalysts were calcined at a certain temperature for 4 h under ambient air .The obtained sample was named as V_2/Al, here, 2 stands for the content of V in mmol unit per 2 g γ-Al_2O_3 carrier.

In the case of industrial EBDH catalysts, potassium is added to Fe_2O_3-based catalyst [1], in this article, γ-Al_2O_3 supported vanadia catalysts were modified with alkali metal (Li, Na, K) and alkaline earth metal (Mg). The promoted catalysts named as V_2Me/Al were prepared by co-impregnation with aqueous solutions of metavanadate (NH_4VO_3) and the corresponding salts of promoter such as LiC_2O_4, Na_2CO_3, CH_3COOK, $Mg(CH_3COO)_2 \cdot 4H_2O$ in oxalic acid (0.25 mol/L) in the molar ratio Me:V = 0.1.

2.2. Evaluation of catalytic dehydrogenation

The EBDH with CO_2 was performed in a Φ6 mm i.d. quartz tube fixed-bed reactor; in each run, a catalyst of 200 mg was placed in the center of the reactor using a quartz glass wool plug. The catalyst was maintained at reaction temperature in a carbon dioxide atmosphere for 10 min before introducing ethylbenzene, the flow rate of feed gas is 50 mL/min and the molar ratio of CO_2 to EB was fixed at 10. The reaction was operated at 450 °C under atmospheric pressure, the reaction products were collected in a U-tube cooled with the mixture of ice and water, then dehydrated and analyzed with HP 6890 gas chromatograph equipped with a FID detector, using a 0.53 mm × 30 m capillary column HP-PLOT Q .The main product of the CO_2–EBDH is styrene and the benzene and toluene is by-products.

After EBDH, the used V_2K/Al catalyst was regenerated for 1 h by introducing air toward the quartz tube, the flow rate of air was 50 mL/min; and then we repeated the experiment using the regenerated catalyst.

2.3. Catalyst characterization

The crystal structures of the catalysts were determined using a Rigaku D/max 2500 X-ray powder diffractometer with monochromated CuK_α radiation in 40 kV/100 mA over a 2θ range from 5 to 85°.

The specific surface area of the sample was determined by the BET method, N_2 adsorption at 77 K in an SORPTMATIC 1990, CE instruments. The obtained isotherms were analyzed by ADP software and pore size distributions were calculated on the basis of BJH method. The TG/DTG analysis was made with a TA instruments from Netzsch, Germany, STA 409C thermogravimetric analyzer. The temperature was programmed to increase at a rate of 10 K/min from room temperature to 1173 K under circulation of dried air in order to investigate the carbon deposition over the catalysts.

The X-Ray photoelectron spectra data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W AlK_α radiation. Samples were analyzed as powders dusted onto double-sided sticky tape in an analysis chamber, the base pressure was about 3×10^{-9} mbar. The binding energy values (BE) were reference to the C_{1s} line at 284.6 eV.

3. Results and discussions

3.1. Catalytic tests

Alkali metals are often mentioned as promoters for industrial catalysts for selective oxidation processes since they afford higher selectivity for partial oxidation reactions [10]. Table 1 displays the effect of various promoters on the catalytic activity in the V_2Me/Al. It is clear that type of additives affects the catalyst activity. The addition of promoters can all increase the selectivity of ST but have different influence on the conversion of EB. The addition of K and Li increase the EB conversion to 15.2% and 14.7%, respectively, the addition of Mg has little increase on the EB conversion, but the addition of Na deteriorated the catalytic activity of V/Al. Cortez *et al.* [10] deemed that the addition of potassium to VO_x/Al_2O_3 catalysts affected the structure and properties of surface vanadium oxide species, potassium removed surface acid sites, generated basic sites through its co-ordination with surface vanadia species. In our experiments, the effect of promoters on the catalytic behavior is not remarkable, this maybe attribute to the lower reaction temperature. Badstube's results [11] can account for this: when the reaction temperature is 623 and 723 K, the effect of promoters is not obvious but when at 823 K, the promotion with alkali or alkali-earth ions lead to a strong increase in ST yield.

Table 2 presents the effect of calcined temperature on the EBDH with a V_2K/Al catalyst. As a function of calcined temperature, the catalysts show different catalytic activity. EB conversion is higher at low calcined temperature than higher calcined temperature; a maximum EB conversion reaches 15.2% at 250 °C while only 8.0% at 550 °C. At all calcined temperature the selectivity of ST are high (>99.0%). Figure 1 shows the

Table 1
Effect of promoters on the catalytic behaviors for CO_2–EBDH*

Catalyst	Conversion of EB (%)	Selectivity (%)		
		Benzene	Toluene	Styrene
V_2/Al	11.8	0.5	1.2	98.3
V_2Li/Al	14.7	0.4	0.7	98.9
V_2Na/Al	11.0	0.3	0.6	99.1
V_2Mg/Al	11.9	0.3	0.5	99.2
V_2K/Al	15.2	0.4	0.4	99.2

*Reaction conditions: T = 450 °C, P = 0.1 MPa, W/F = 45 $g_{cat} \cdot h$/mol-EB, flow rate of feed gas = 50 ml/min, molar ratio of CO_2/EB = 10, Data were acquired after reaction lasted for 1 h.

Table 2
Effect of calcined temperature on the V_2K/Al activity and SSA

Catalysts	Conversion (%)	Selectivity (%)	SSA* (m^2/g)	Pore volume (cm^3/g)	Mean pore radius (nm)	Maximum pore radius (nm)
$V_2K/Al250$	15.2	99.8	147.9	0.3	6.5	5.7
$V_2K/Al350$	12.6	99.4	140.2	0.3	7.1	6.2
$V_2K/Al450$	11.1	99.6	142.1	0.4	6.6	5.9
$V_2K/Al550$	8.0	99.0	140.0	0.3	6.8	6.0

Note: SSA-specific surface area.

XRD pattern of the catalysts after different calcined temperature, we did not find the peak corresponding to other materials except the peak of γ-Al_2O_3. It can be explained that vanadium species have a good dispersion in the support surface, smaller V_2O_5 crystallites may also be present, but they cannot be detected by diffraction methods because of their low concentration, poor crystallinity, or small numbers of unit cells [12]. The BET specific surface area values presented in table 2 indicate that the change of catalytic behavior may attribute to the different specific surface area and pore size of catalysts after different calcined temperature. Catalyst calcined at 250 °C had the largest surface area and the highest catalytic behavior.

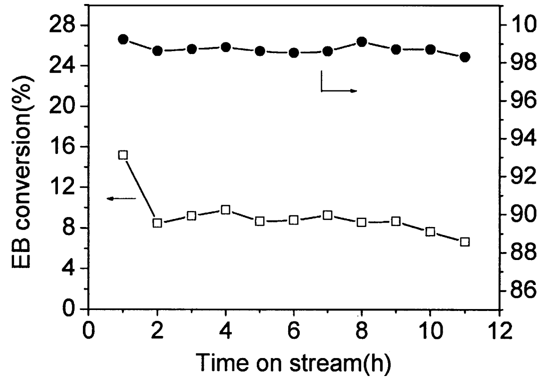

Figure 2. Catalytic activity of V_2K/Al with time-on-stream.

3.2. Catalysts stability

Based on the catalytic activities of different catalysts, V_2K/Al calcined 250 °C was chosen to be evaluated further. Figure 2 shows EB conversion, ST selectivity as a function of reaction time at a reaction temperature of 450 °C in the presence of carbon dioxide over V_2K/Al catalyst. The ST selectivity kept a high value(>98%), the initial EB conversion during the reaction for 1 h was highest (15.2%), with an increasing reaction time, it decreased to 8.5%, after a run of 11 h the ST yield decreased to 6.6%. Table 3 shows the specific surface area of the catalysts before and after the reaction, it is clearly showed the decrease of the surface area and pore volume after the catalytic reaction, it seems to be due to the coke deposition during the dehydrogenation, and such deposition may be a cause of deactivation of the catalyst.

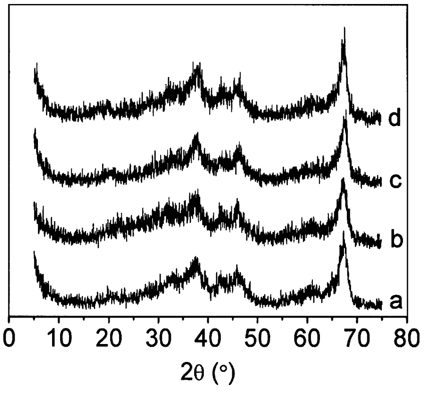

Figure 1. XRD pattern of catalyst on different calcined temperature: (a) 250 °C, (b) 350 °C, (c) 450 °C, (d) 550 °C.

Figure 3 presents the TG/DTG profile of V_2K/Al from 1 and 11 h reactions. There is two weight loss peaks occurring in TG/DTG profile, the first one is corresponding to the loss of water and the second one can be attributed to the weight of carbonaceous deposit during the dehydrogenation, the weight loss percent of V_2K/Al catalyst after dehydrogenation of 1 and 11 h were 6.5% and 7.0%, respectively. We also detected that the color of used catalysts were black, after TG/DTG analysis the catalyst became green again like fresh catalyst, so we further investigated the activity of regenerated V_2K/Al catalyst used for 1 h. After regeneration by air, the catalytic activity of V_2K/Al was resumed, 13.5% EB conversion and 97.6% ST selectivity were received. This indicated that the catalyst could be regenerated easily.

The XRD pattern of fresh and used catalyst are compared in figure 4. The used V_2K/Al catalysts present

Table 3
SSA analysis of fresh and used V2K/Al catalyst

Catalysts	SSA (m^2/g)	Pore volume (cm^3/g)	Mean pore radius (nm)	Maximum pore radius (nm)
Fresh V_2K/Al	147.9	0.3	6.5	5.7
Used V_2K/Al (1 h)	132.1	0.3	6.9	6.0
Used V_2K/Al (11 h)	129.1	0.3	6.6	6.0

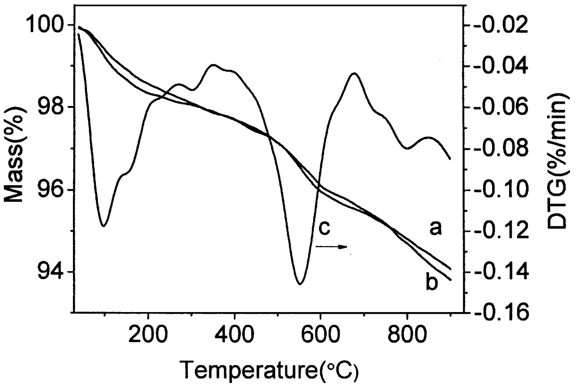

Figure 3. TG profile of V_2K/Al after CO_2–EBDH reaction 1 h (a) and 11 h (b) and DTG profile of V_2K/Al after CO_2–EBDH for 1 h (c).

distinct peak of VO_2 crystallites and the intensity of V_2K/Al used for 1 h are higher than that for 11 h, these imply that part of the oxidized vanadium species on the surface were reduced into VO_2 phase and the vanadium species migrated and aggregated during the catalytic reaction.

The corresponding XPS spectra of V_2K/Al catalyst before and after the CO_2–EBDH reaction are shown in figure 5 and table 4. For the fresh V_2K/Al catalysts, its binding energy for V $2p_{3/2}$ (517.2 – 517.6 eV) is corresponded to V^{5+} species [13], revealing that the fresh catalyst possess the highest oxidation states of V, the result of the used (1 h) V_2K/Al shows that the corresponding parameters of V $2p_{3/2}$ are similar to the fresh catalyst, but full width at half maximum (FWHM) of the V $2p_{3/2}$ for the catalysts is increased relative to the fresh V_2K/Al, from 3.23 to 3.52, indicating the reduction of surface vanadium species during the reaction. From the data of the used (11 h) catalyst, the binding energy value is shifted from 517.40 to 516.68 eV, the corresponding FWHM increases from 3.23 to 3.56 eV, suggesting that the catalyst surface undergo reduction of vanadium oxides. Moreover, we calculated the C/Al and V/Al atomic ratio, result showed that the C/Al increased and the V/Al decreased after reaction for 1 and 11 h. Increase of C/Al implied that the producing of coke deposited in the dehydrogenation, increase of V/Al suggested the migration of active vanadium species, and these results are agreed with the TG and XRD analysis.

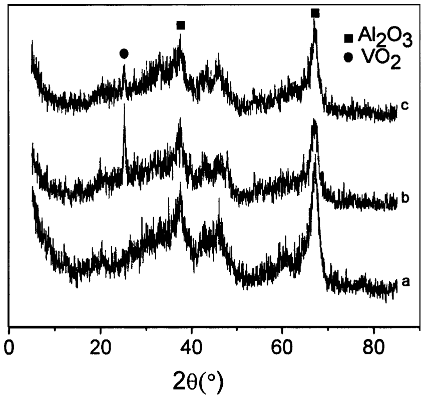

Figure 4. XRD pattern of fresh (a) and used V_2K/Al catalyst for 1 h (b) and 11 h (c).

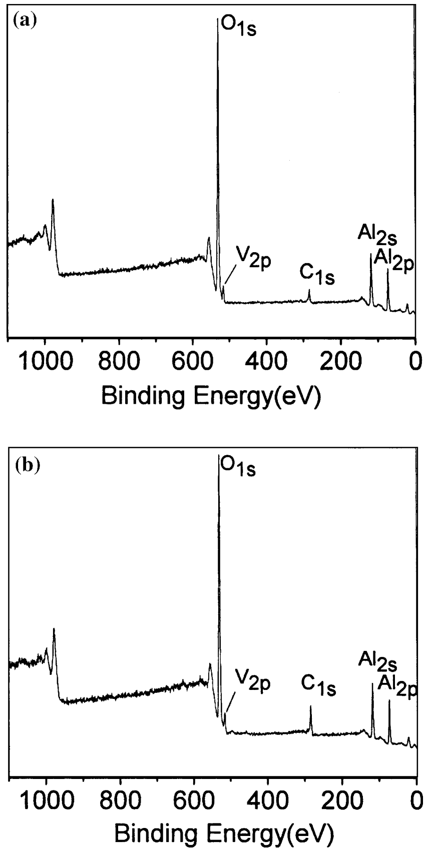

Figure 5. XPS patterns of V_2K/Al (a) fresh, (b) used catalyst for 11 h.

There are several possible causes for deactivation of the catalyst [14]: (1) by-products of the dehydrogenation (hydrogen, carbon monoxide and so on) reduce active species to inactive species that adhere to the catalyst; (2) active species are covered by deposited coke; and (3) active species are gradually poisoned with water generated by the reverse water-gas shift reaction ($H_2 + CO \rightarrow H_2O + CO_2$). In our present study, we assumed that the deactivation of the catalyst during the dehydrogenation of EB in the presence of carbon dioxide might be caused by the evidence (1) and (2).

Table 4
XPS spectra of fresh and used catalyst

Catalyst		V2p$_{3/2}$ (eV)		C/Al	V/Al
		BE	FWHM		
V_2K/Al	Fresh	517.40	3.23	0.13	0.094
V_2K/Al	Used for 1 h	517.40	3.52	0.66	0.012
V_2K/Al	Used for 11 h	516.68	3.56	0.59	0.005

BE – binding energy; FWHM – full with at half maximum.

Catalytic behavior for selective oxidation on vanadium oxide-based catalysts is related with the redox properties of vanadium species [15]. Sakurai *et al.* [6] and Park *et al.* [16] studied the performance of V/AC, V/MgO and V/Al_2O_3 catalysts in the CO_2–EBDH and proposed that the reaction proceeded according to the redox mechanism. Sun *et al.* [9] also showed that over V/Al_2O_3 the redox cycle is crucial for the CO_2 activation. Based on our above discussions, it can be concluded that the catalytic reaction over V_2K/Al followed the redox cycle.

4. Conclusions

Alumina-supported vanadium oxides (V_2K/Al) were found to be an effective catalyst for the CO_2–EBDH in a lower temperature. The promoters have effect on the activity of V_2/Al at 450 °C, and V_2K/Al calcined at 250 °C had a better catalytic reactivity than that calcined at higher temperature. The catalyst stability was also discussed, the reduction of surface vanadium species and coke deposition maybe the major reason for the catalyst deactivation, after regeneration the catalytic activity of V_2K/Al can be resumed as 87% as the fresh one.

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