Oxidative dehydrogenation of ethylbenzene with carbon dioxide over metal-doped titanium oxides

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Various metal-doped (Fe, V, Zr, Mg) titanium oxides were prepared by an acid-catalyzed sol–gel method and their properties as catalysts were investigated for oxidative dehydrogenation of ethylbenzene in the presence of carbon dioxide. The characterization techniques, XRD, BET, TGA were employed to analyze the features of catalyst. Fe_3Ti catalyst was found to be quite effective among the catalysts tested at 823 K, 39.8% ethylbenzene conversion and 98% styrene selectivity were acquired.

KEY WORDS: metal-doped titanium oxides catalyst; oxidative dehydrogenation of ethylbenzene; carbon dioxide.

1. Introduction

Styrene is one of the most important starting compounds for the synthesis of many polymers, about 13 million tons of styrene are annually produced all over the world, and 90% are commercially produced by the dehydrogenation of ethylbenzene (EBDH) on Fe–K-based catalysts at 873–973 K [1,2]. However, EBDH is thermodynamically limited and, moreover, it is a very energy consuming process because of the required excess of superheated steam.

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. For the greenhouse effects and the increase of CO_2 release, catalytic conversion of CO_2 has been extensively studied during the last decade. Recently, carbon dioxide was used as a soft oxidant in the oxidative dehydrogenation of ethylbenzene (CO_2-EBDH). The process could be effective in respect of utilization of carbon dioxide resources, being energy-saving and environmentally friendly [3,4].

Since the commercial Fe–K-based catalysts are not effective for dehydrogenation of ethylbenzene in the presence of CO_2, the study of high-performance catalysts has received many concerns, and several effective catalysts were reported [5–15], such as Fe_2O_3/γ-Al_2O_3 [5], V/MgO [12], Li/Fe_2O_3/AC and Sb/V_2O_5/AC [14]; most of them are supported catalysts, and some mixed oxides catalysts prepared by impregnation or deposition method. Due to the facile control of catalyst characteristics, such as elemental compositions, surface areas and pore size distributions in single-step preparation ways, the potential of the sol–gel method to prepare microporous and mesoporous structures in solids has significant advantages over other preparation procedures. Titanium-oxide-based catalysts are noticeably studied in heterogeneous catalysis, especially in selective oxidative reaction as in the light of its attractive physical and chemical properties by (thermal, mechanical and chemical resistance). In our previous work, the catalytic performance of porous mixed oxides Cr_xTi prepared with acid-catalyzed sol–gel method has been investigated in the oxidative dehydrogenation of ethylbenze under the circulation of synthetic air [16].

In this paper, various metal-doped titanium oxides were prepared by an acid-catalyzed sol–gel method as potential catalysts for CO_2-EBDH. A metal-doped titanium oxide is described with the general formula M_xTi, where M is the element of metal, x is the molar percent of M. Fe was found to be the best among four different metal active components. The preparation and reaction conditions were investigated in details especially their influence on the activity of Fe_xTi in CO_2-EBDH.

2. Experimental

2.1. Catalyst preparation

Various mixed oxides M_xTi (x ranged from 1 to 7 mol%) were prepared by an acid catalyzed sol–gel process in analogy to the following procedure. For preparation of an iron/titanium oxide Fe_xTi as an example, $Ti(OiPr)_4$ was dissolved in ethanol and stirred in a 250 mL PP-beaker for 15 min, then 12 and 8 N HCl

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Table 1
Catalytic behavior of various metal-doped titanium oxides for CO_2-EBDH

Catalyst	EB conversion	Yield (%)			ST selectivity
	(%)	Benzene	Toluene	Styrene	(%)
TiO_2	6.4	0	1.1	5.4	83.1
Fe_3Ti	19.3	0.6	0	18.6	96.4
V_3Ti	11.6	0	0	11.6	100.0
Zr_3Ti	9.9	0	1.1	8.8	89.3
Mg_3Ti	10.0	0	0.9	9.0	90.6

Note: Reaction conditions: $T = 823$ K, $P = 0.1$ MPa, W/F = 40 g_{cat} h/mol, flow rate of feed gas = 50 mL/min, molar ratio of CO_2/EB = 11; data were acquired after reaction lasted for 1 h.

were added in turn. Iron(III)-chloride hexahydrate was dissolved in ethanol, stirred, and slowly poured into the above beaker with stirring. Then the beaker was covered with polypropylene-film and stored overnight under stirring until the sol converted into a gel. After drying, the gel were calcined according to the temperature program:

$$RT \xrightarrow{0.5\,K/min} 338\,K(180\,min) \xrightarrow{0.5\,K/min} 823\,K(180\,min) \xrightarrow{2\,K/min} RT$$

2.2. Reaction and analytical procedures

The catalytic reaction was performed in a Φ 6 mm i.d. quartz tube reactor, and 200 mg of catalyst were used in each run. The catalyst was maintained at reaction temperature in a carbon dioxide atmosphere for 10 min before introducing ethylbenzene (EB), the flow rate of feed gas is 50 mL/min and the molar ratio of CO_2 to EB was fixed at 11. The reaction was operated from 623 to 823 K at atmospheric pressure, the reaction products were collected in a U-tube cooled with the mixture of ice and water, then analyzed with a gas chromatograph (HP 6890) equipped with a FID detector, using a 0.53 mm × 15 m capillary column HP-PLOT/Al_2O_3 "M" deactivated.

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 (40 kV/100 mA) radiation. The specific surface area of the sample was determined by the BET method, i.e., N_2 adsorption at 77 K in an SORPTMATIC 1990 (CE instruments, Italy). The obtained isotherms were analyzed by ADP software and pore size distributions were calculated on the basis of BJH method. The TG/DTA analysis was made with a TA instruments (Netzsch, Germany) STA 409C thermogravimetric analyzer. The temperature was programmed to increase at a rate of 10 K/min from room temperature to 1073 K under circulation of dried air.

3. Results and discussion

3.1. Catalytic activity

To recognize better applicability of CO_2 as the oxidative reactant, four metals (Fe, V, Zr, Mg) were chosen in this study, the catalytic results over various metal-doped titanium oxides catalysts were collected in table 1. Benzene and toluene were detected as by-products. The pure TiO_2 (also prepared in sol–gel method) showed a very low activity, only an EB conversion of 6.45% and ST selectivity of 83.1% was obtained at 823 K. Among these catalysts, Fe_3Ti showed the best activity, at 873 K, an EB conversion of 19.3% and ST selectivity of 96.4% was observed over it, which was chosen for subsequent testing.

3.2. Effect of Fe content in Fe_xTi catalysts on reactivity

The catalytic activity of Fe_xTi catalysts with various Fe contents is shown in figure 1. It was clear that the content of Fe had a strong influence on the catalytic activity, EB conversion increased with the increase of Fe content and reached the highest value when Fe content was equal to 3 mol%, and further increase of Fe content led to a decrease of EB conversion. Additionally, the highest selectivity (99.3%) to styrene was also observed

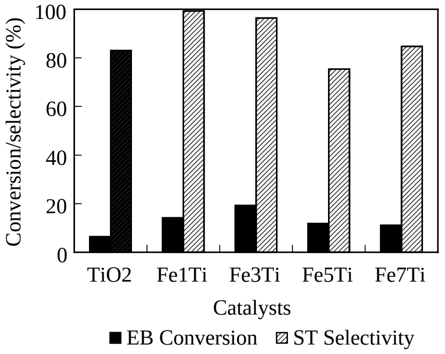

Figure 1. Activity of Fe_xTi catalysts with various Fe contents: $T = 823$ K, $P = 0.1$ MPa, W/F = 40 g_{cat} h/mol, flow rate of feed gas = 50 mL/min, CO_2/EB = 11, data acquired after reaction lasted for 1 h.

Table 2
The specific surface area, pore volume and pore size of Fe_xTi catalysts

Catalysts	EB conv. (%)	ST yield (%)	SSA (m^2/g)	PV (cm^3/g)	Mean pore dia. (nm)	Max. pore dia. (nm)
TiO_2	6.4	5.4	21.7	0.1	3.2	2.7
Fe_1Ti	14.2	14.1	98.0	0.3	3.3	3.3
Fe_3Ti	19.3	18.6	61.1	0.2	3.4	3.7
Fe_5Ti	11.8	8.9	37.4	0.1	3.8	3.5
Fe_7Ti	11.1	9.4	57.4	0.2	3.3	2.6

Note: SSA – specific surface area; PV – pore volume.

with Fe_1Ti, an excess of Fe content is harmful to both EB conversion and ST selectivity. With an increase of Fe content in Fe_xTi catalysts, there exists a highest value of EB conversion, 19.3%, over Fe_3Ti.

Analysis of the physical properties of Fe_xTi catalysts is shown in table 2, we found that pure TiO_2 showed a lower specific surface area, and the addition of Fe to catalysts led an increase in the BET surface area and in the pore volume; pore characteristics such as mean pore diameter and maximum pore diameter were also changed by the addition of Fe, which might tell us that the addition of Fe would suppress the sintering of the catalyst, change the pore character and increase the total pore volume. Fe_1Ti catalyst has the greatest specific surface area among the investigated catalysts and the smallest pores, the EB dehydrogenation reaction over/in it would last relatively longer time in comparison with other catalyst, the lower EB conversion 14.2%, was acquired. For the condition of Fe_3Ti catalyst with 3.4 nm mean pore diameter, EB conversion was obviously increased to 19.3%. Here it should be mentioned, that higher specific surface area and concentrated pore distribution (3.2–3.8 nm) help to increase the selectivity of styrene and the conversion of ethylbenzene, and the catalytic activity of catalyst has a strong relation with itself available specific surface area and pore distribution.

In addition, all Fe_xTi catalysts showed no diffraction peaks of iron species (see figure 2), which proved that iron species were highly dispersed in TiO_2 support. Ti crystal structure in Fe_1Ti was entirely anatase, the rutile phase increased with an increase of Fe loading level from 1 to 7 mol%; it was almost rutile phase in Fe_7Ti catalyst, which showed us that Fe played an important role during TiO_2 crystallization. At the same time, the styrene selectivity decreased with the increase of rutile phase in catalysts, at 823 K, the styrene selectivity over the catalyst Fe_1Ti was 99.3%, and decreased to 84.7% over Fe_7Ti. Thus, a suitable ratio of anatase phase to rutile phase in Fe_xTi was beneficial to the dehydrogenation.

3.3. *Influence of reaction temperature*

The effect of reaction temperature on the styrene yield was shown in figure 3. The ST yield of all catalysts was very low at low reaction temperature, and increased with its increase. Pure TiO_2 (prepared in acid catalyzed sol–gel method) showed a poor activity, over which the ST yield was the lowest at any investigated temperature. The ST yield obviously increased after Fe was doped. The addition of Fe improved the activity of TiO_2. Obviously, Fe was an active component for this reaction. Among the investigated catalysts with different Fe contents, 3 mol% Fe doped-titanium oxide catalyst showed the best selectivity to ST, the ST yield over Fe_3Ti was 1.07% at 623 K, however, reached 18.6% at 823 K. It has been proved by the thermodynamics analysis that with an increase of reaction temperature

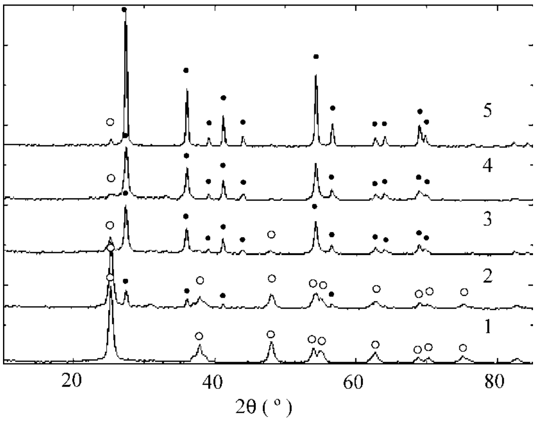

Figure 2. XRD pattern of Fe_xTi catalysts (1 – Fe_1Ti, 2 – Fe_3Ti, 3 – Fe_5Ti, 4 – Fe_7Ti, 5 – TiO_2, ○ – Anatase TiO_2, ● – Rutile TiO_2).

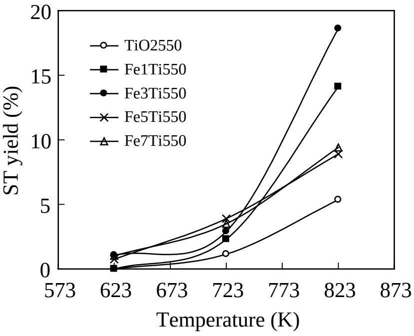

Figure 3. Effect of reaction temperature on the styrene yield.

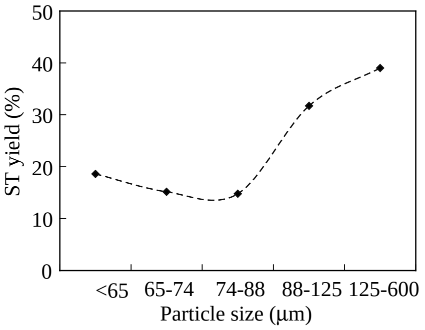

Figure 4. The dependence of Fe_3Ti particle size on EB conversion and ST selectivity.

the EB and CO_2 conversion and the ST yield would increase but the ST selectivity would decrease [14], therefore, the feasible reaction temperature in this study is 823 K. Nonetheless, further increase of Fe contents was not benefit to the ST yield at higher reaction temperature. At 823 K, the ST yield over Fe_5Ti and Fe_7Ti was 9.4% and 8.9% correspondingly. It gives us a hint that there is a suitable ratio of Fe to Ti for the preparation of Fe_xTi catalyst for EB selective oxydehydrogenation.

3.4. *Influence of particle size*

The particle size of catalysts had a strong influence on ST yield in our experiment. Five different particle sizes (65–600 μm) were obtained from a freshly prepared catalyst by grinding in a mortar, milling in a ball mill and sieving. During preceding this procedure, all the sieve fractions have been controlled by Malvern Mastersizer 2000. Figure 4 shows the effect of particle size on the reaction under identical reaction conditions using Fe_3Ti catalyst. In all investigated particle sizes experiments, the effect of particle size on the ST selectivity was slight but the EB conversion was great. It could be seen that the ST yield over Fe_3Ti with particle size about 74–88 μm was only 14.8% (14.9% EB conversion and 99% ST selectivity respectively), however, it reached 39.0% (39.8% EB conversion and 98% ST selectivity respectively) when the particle size was 125–600 μm. A common problem is that smaller particle size would tend to adhere to each other by electrostatic effects, and lead to the bigger resistance for the contact of EB with catalyst, once the loading catalyst in the reactor was uneven, it would easily form "canal" with smaller resistance, EB passed through this "canal" and then EB conversion decreased. Bigger particle size was more beneficial to the dehydrogenation of EB over Fe_3Ti catalyst and the release of ST produced was swiftly swept from the surface of catalyst in this study. To avoid the above phenomena happened, the reactor structure or the loading catalyst way should be improved further.

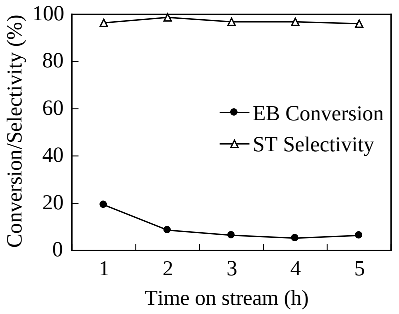

Figure 5. Catalytic activity of EB dehydrogenation as a function of time-on-stream over Fe_3Ti.

3.5. *Catalysts stability*

Figure 5 shows the change of the EB conversion and ST selectivity with time on stream over Fe_3Ti at 823 K. During the reaction process, the ST selectivity kept a very high value (>98%), however, the initial EB conversion during the reaction for 1 h is very high (19.4%) and sharply decreased to 8.6% after dehydrogenation for 2 h then greatly became stable with time on stream. The deactivation of catalyst was one of the major and complicated problems in CO_2-EBDH.

Figure 6 presents the TGA profile of Fe_3Ti after dehydrogenation for 1 and 5 h, which was taken in the presence of oxygen. There was an obvious weight loss occurring at about 500–700 K in TGA profile; the loss in the TGA profile corresponded to the weight of coke deposited in the dehydrogenation, the weight loss percent of Fe_3Ti catalyst after dehydrogenation for 1 and 5 h was 1.18% and 3.08% respectively, which indicated that coke deposited increased with time-on-stream. The DTA profile (figure 7) of Fe_3Ti after dehydrogenation for 5 h shows a distinct exothermal peak caused by coke burning in the same temperature range 500–700 K.

In principle, introducing CO_2 would reduce coke production on the surface of the catalyst according to the reaction (1),

$$C + CO_2 \rightarrow 2CO \tag{1}$$

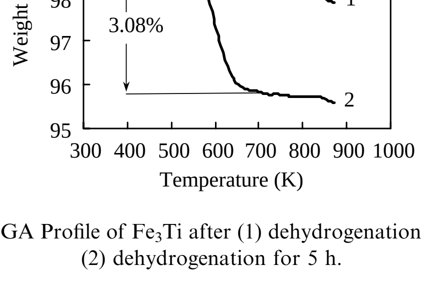

Figure 6. TGA Profile of Fe_3Ti after (1) dehydrogenation for 1 h and (2) dehydrogenation for 5 h.

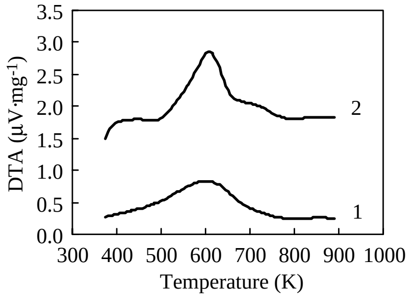

Figure 7. DTA Profile of Fe_3Ti after (1) dehydrogenation for 1 h and (2) dehydrogenation for 5 h.

In fact, the two parallel reactions of coking and decoking proceeded during EB dehydrogenation in the presence of CO_2. In the starting stage, the velocity of coking was faster than decoking, which led to the deactivation of the catalysts, and the catalyst activity could be stable when the coking and decoking reach an equilibrium [14]. For Fe_3Ti, after the decoking, the catalyst activity was resumed to some extent with an EB conversion about 5%.

This finding clearly indicated that the deactivation of the catalyst during oxidative dehydrogenation of ethylbenzene with carbon dioxide was mostly caused by coke deposition. However, the deactivation mechanism was perhaps more complicated and the coking might be only one of the reasons, further investigation are necessary in the future.

4. Conclusions

A mixed-oxides catalyst Fe_xTi prepared by an acid-catalyzed sol–gel method was effective for the dehydrogenation of EB in the presence of CO_2, a high ST yield of 39.0% was observed at 823 K. The surface as well as bulk structure of Fe_xTi catalysts were affected by the doping level of Fe. A suitable concentration of the anatase phase in the bulk structure was beneficial to EB dehydrogenation, the active species might be highly dispersed in titanium matrix. Coke deposition was one of the major causes that led to deactivation of the Fe_xTi catalysts during the dehydrogenation.

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