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Regeneration behaviors of Fe/Si-2 and Fe–Mn/Si-2 catalysts for C_2H_6 dehydrogenation with CO_2 to C_2H_4

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The catalytic performance of Fe/Si-2 and Fe–Mn/Si-2 catalysts for conversion of C_2H_6 with CO_2 to C_2H_4 was examined in a continuous-flow and fixed-bed reactor. The results show that the Fe–Mn/Si-2 catalyst exhibits much better reaction activity and selectivity to C_2H_4 than those of the Fe/Si-2 catalyst. Furthermore, the coking–decoking behaviors of these catalysts were studied through TG. The catalytic performances of the catalysts after regeneration for conversion of C_2H_6 or dilute C_2H_6 in FCC off-gas with CO_2 to C_2H_4 were also examined. The results show that both activity and selectivity of the Fe–Mn/Si-2 catalyst after regeneration reached the same level as those of the fresh catalyst, whereas it is difficult for the Fe/Si-2 catalyst to refresh its reaction behavior after regeneration.

Keywords: C_2H_6, CO_2, Fe/Si-2 catalyst, regeneration

1. Introduction

The production of C_2H_4 has been depending on the pyrolysis of gaseous alkane and liquid petroleum products. With the growing need of C_2H_4, catalytic chemists have been trying to explore alternative routes of producing C_2H_4, such as preparing C_2H_4 from synthesis gas or CH_3OH, coupling of CH_4 oxidation and C_2H_6 dehydrogenation, etc. [1–7]. In order to obtain C_2H_4 from C_2H_6, the coupling reaction of C_2H_6 dehydrogenation and CO_2 hydrogenation as a new way has been reported [7,8]. Its advantage is that the reaction of C_2H_6 dehydrogenation with CO_2 to C_2H_4 can be performed at a relatively lower temperature with achievement of a much higher selectivity for C_2H_4. Of course, the key problem is the development of a new catalyst with desirable behaviors. A silicate-2 zeolite supported Fe–Mn catalyst (denoted as Fe–Mn/Si-2) with high conversion of C_2H_6 and high selectivity for C_2H_4 was developed recently, by means of screening the support and optimization of the metal active component [7,8].

In the present paper, the catalytic performances of Fe/Si-2 and Fe–Mn/Si-2 for conversion of C_2H_6 with CO_2 to C_2H_4 have been examined. The deactivation and regeneration of these catalysts have also been investigated by TG-DTG. Some interesting information is provided from these results, which are very necessary and very important for future perfecting the process for conversion of C_2H_6 with CO_2 to C_2H_4.

2. Experimental

2.1. Preparation of the catalyst

The catalysts used were silicalite-2 zeolite supported Fe catalysts (denoted as Fe/Si-2) and Fe–Mn catalysts (Fe–Mn/Si-2). Under vacuum conditions, supported Fe/Si-2 catalysts were prepared by impregnating a solution with a given amount of $Fe(NO_3)_3$ onto a silicalite-2 zeolite and Fe–Mn/Si-2 catalysts were prepared by impregnation of a solution with a given amount of $Fe(NO_3)_3$ and $Mn(NO_3)_2$ onto a silicalite-2 zeolite. After being dried at 400 K for 8 h and calcined at 800 K for 10 h, the catalysts were cooled, crushed and screened. Catalyst samples with a size of ∅1.2 mm × 2.5 mm were tested in the C_2H_6 dehydrogenation with CO_2 to C_2H_4.

2.2. Reaction performance of the catalyst

The catalytic performances of catalysts were evaluated in a continuous-flow and fixed-bed reactor made of stainless steel with catalyst loading of 6 ml. Reaction conditions were set as follows: reaction temperature 780–800 °C, $C_2H_6/CO_2 = 1:1$ (mole ratio), pressure 0.1 MPa and GHSV 1000 h^{-1}. Analysis of product composition was performed on-line in a gas chromatograph with a TCD detector.

2.3. Coking–decoking measurement of the catalyst

Coking and decoking measurements were performed on a Shimadzu DT-30 type thermoanalyzer with a range of ±10 mg, heating rate of 20 °C/min, chart speed of

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5 mm/min. Coking was performed under conditions of isothermal temperature of 780 °C and C_2H_6/CO_2 ratio of 1/1. Decoking was carried out under heating in a temperature-programmed mode with flowing air.

3. Results and discussion

3.1. Catalytic performance of Fe/Si-2 and Fe–Mn/Si-2 catalysts

In the present paper, a new kind of silicalite-2 zeolite supported Fe–Mn catalyst is reported for the production of C_2H_4 from C_2H_6 with CO_2 as an oxidant. The dehydrogenation of C_2H_6 by the unconventional oxidant CO_2 is an interesting process from both the scientific and practical points of view [6,8]. By studying the reaction mechanism of C_2H_6 with CO_2 and the reaction thermodynamics as well as the reaction dynamics [9,10], it has been shown that the reaction of C_2H_6 and CO_2 to C_2H_4 is a combination of ethane dehydrogenation and CO_2 hydrogenation. That is to say, this reaction consists of two consecutive coupling reactions. Generally, the coupling reaction of C_2H_6 dehydrogenation and CO_2 hydrogenation for conversion of C_2H_6 to C_2H_4 can be represented as follows:

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2$$
$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

And, the reaction of H_2 from C_2H_6 dehydrogenation with CO_2 can continuously shift C_2H_6 to C_2H_4, thereby enhancing the conversion of C_2H_6 and the selectivity of C_2H_4.

The evaluated results of catalytic performances for Fe/Si-2 and Fe–Mn/Si-2 catalysts under conditions of reaction temperature of 800 °C, reaction pressure of 0.1 MPa, gas space velocity of 1000 h^{-1} and $C_2H_6/CO_2 = 1:1$ are summarized in table 1, from which it can be observed that Fe–Mn/Si-2 catalysts possess better catalytic performance than the Fe/Si-2 catalysts. When Fe loading is in the range 5–9%, with an increase of Fe content not only the conversion of C_2H_6 and CO_2 increased obviously, but the selectivity for C_2H_4 also increased. Especially with the addition of a Mn promoter onto the Fe/Si-2 catalyst, both the reaction activity and C_2H_4 selectivity were improved greatly. It can be found from table 1 that when Mn is loaded in the range 2–9%, the increase of Mn content is more beneficial to increasing the conversion of CO_2 and selectivity for C_2H_4 and to reducing the production of CH_4. In general, for Fe–Mn/Si-2 catalyst with addition of Mn promoter, as high as 93% of C_2H_4 selectivity is obtained with more than 66% of ethane conversion. By the way, at the beginning reaction, the conversion of C_2H_6 is much higher and the selectivity of C_2H_4 is relatively lower; in about 3 h, a stable state of catalytic behavior is reached for the Fe–Mn/Si-2 catalyst. Furthermore, from the results shown in figure 1, it is clear that Fe–Mn/Si-2 has much better catalytic reaction stability for ethane dehydrogenation with CO_2 than Fe/Si-2. In addition, owing to the increase of conversion of CO_2, the H_2/CO molecule ratio has the tendency to decrease. Therefore, it can be considered that the promotions of Mn mainly lie in raising the conversion of CO_2 and selectivity for C_2H_4 and improving the catalytic stability greatly.

Table 1
The catalytic performance of ethane dehydrogenation with CO_2 as an oxidant over Fe/Si-2 and Fe–Mn/Si-2 catalysts.[a]

Catalyst	Conversion (%)		Selectivity (%)		H_2/CO
	CO_2	C_2H_6	CH_4	C_2H_4	
5Fe/Si-2	18.2	57.2	29.4	70.6	1.7
9Fe/Si-2	24.7	62.1	26.0	74.0	1.4
9Fe–2Mn/Si-2	26.5	61.2	21.5	78.5	1.2
9Fe–9Mn/Si-2	39.1	68.6	7.7	92.3	0.9

[a] Reaction conditions: 800 °C, 0.1 MPa, 1000 h^{-1}, $C_2H_6/CO_2 = 1:1$.

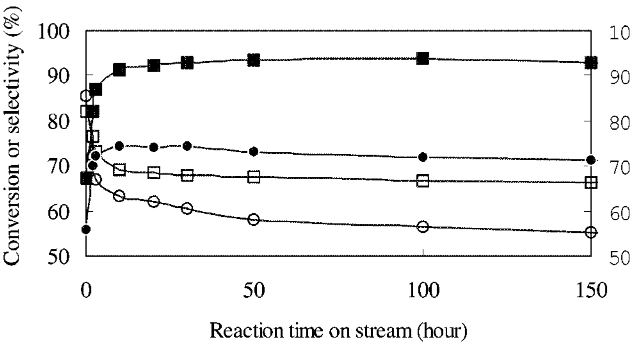

Figure 1. The performances of Fe/Si-2 and Fe–Mn/Si-2 catalysts for C_2H_4 production from C_2H_6/CO_2 reaction with reaction on stream. Fe–Mn/Si-2 catalyst: (■) C_2H_4 selectivity, (□) C_2H_6 conversion. Fe/Si-2 catalyst: (●) C_2H_4 selectivity, (○) C_2H_6 conversion.

3.2. Coking on Fe/Si-2 and Fe–Mn/Si-2 catalysts

By investigating the influence of coking reaction time on the coking behaviors Fe/Si-2 and Fe–Mn/Si-2 catalysts under conditions of reaction temperature 780 °C, $C_2H_6/CO_2 = 1:1$, it can be observed, from the isothermal coking TG curves of the catalysts (figure 2), that the coking amounts of C_2H_6 reaction with CO_2 both on Fe/Si-2 and Fe–Mn/Si-2 increase with coking reaction time on stream. Within 1 h, the relationship between the coking and time for the catalysts is a straight line basically. But at the same time the amount of carbonaceous deposition on Fe/Si-2 is by far greater than that on the Fe–Mn/Si-2 catalyst. That is to say, with the addition of Mn promoter, the coking deposition on the Fe/Si-2 catalyst is prohibited greatly. By investigating the factors influencing coking behavior, it has been shown that by the modification of Fe/Si-2 by the Mn promoter, coke carbonaceous on the Fe/Si-2 catalyst becomes more active to react with CO_2 forming CO, resulting in the decrease of carbonaceous deposition [11].

In order to explore the coking performance of the C_2H_6 reaction with CO_2 on Fe/Si-2, the coking curves can be represented by Voorhie's empirical formula:

$$C = K_c t^m, \tag{1}$$

where C is the amount of carbonaceous deposition, K_c is the coking reaction rate constant, t is the coking reaction time, and m is the coking reaction time exponent. The logarithmic form of equation (1) is

$$\log C = \log K_c + m \log t. \tag{2}$$

According to the relationship between $\log C$ and $\log t$, the plot of $\log C$ versus $\log t$ should be a straight line. The values of the coking reaction time exponent (m) and coking reaction rate constant (K_c) can be easily obtained from the slope and intercept of the straight line, respectively. The results of measurement of coking deposition on Fe/Si-2 and Fe–Mn/Si-2 catalysts during C_2H_6 reaction with CO_2 are reported in tables 2 and 3.

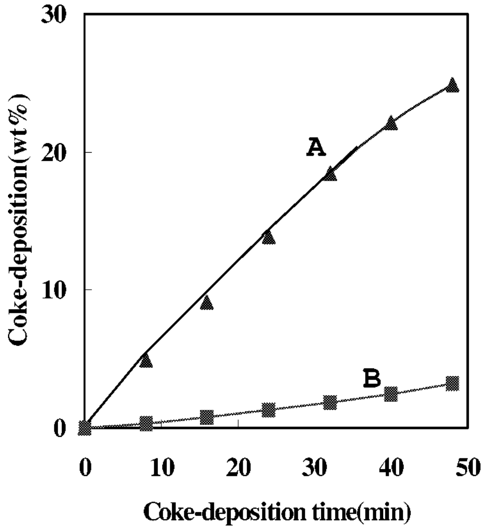

Figure 2. Isothermal coking TG curves on Fe/Si-2 (▲) and Fe–Mn/Si-2 (■) catalysts at 780 °C.

From the results of the coking deposition on Fe/Si-2 and Fe–Mn/Si-2 catalysts with coking reaction time on stream, the value of the coking reaction time exponent (m) and coking reaction rate constant (K_c) can be calculated according to equation (2), as listed in table 4.

Thus the relationship between the coking deposition amount and coking reaction time on stream is expressed as follows:

for 9Fe/Si-2 catalyst,

$$C = 7.12 \times 10^{-3} t^{0.92}; \tag{3}$$

for 9Fe–9Mn/Si-2 catalyst,

$$C = 2.18 \times 10^{-4} t^{1.28}. \tag{4}$$

3.3. Decoking on Fe/Si-2 and Fe–Mn/Si-2 catalysts

3.3.1. Decoking behaviors of deactivated catalysts in air

Decoking TG-DTG curves of deactivated catalysts are shown in figure 3. The results for decoking reaction order and decoking reaction activation energy can be calculated by the Broido method [12] following the deduced procedure:

when $n = 1$,

$$\ln \ln(1-\alpha)^{-1} = -\frac{E/R}{T} + A, \tag{5}$$

when $n \neq 1$,

$$\ln\left\{\frac{[1-(1-\alpha)]^{1-n}}{1-n}\right\} = -\frac{E/R}{T} + B, \tag{6}$$

where α is the decoking fraction, n is the decoking reaction order, which can be calculated by the method shown in the literature [13], E is the decoking reaction activation energy,

Table 2
The results of measurements of coke deposition at various times on 9Fe/Si-2 catalyst.

Sample weight (mg)	Reaction time (min)	Coke deposition (mg)	Coke deposition (%)	$\log C$	$\log t$	
40.70	8	2.00	4.91	−1.3089	0.9030	$m = 0.92$
	16	3.70	9.09	−1.2041	1.2041	$K_c = 7.12 \times 10^{-3}$
	24	5.64	13.85	−0.8585	1.3802	$r = 0.9989$
	32	7.50	18.42	−0.7347	1.5051	
	40	9.00	22.11	−0.6554	1.6020	
	48	10.14	24.91	−0.6036	1.6812	

Table 3
The results of measurement of coke deposition at various times on 9Fe–9Mn/Si-2 catalyst.

Sample weight (mg)	Reaction time (min)	Coke deposition (mg)	Coke deposition (%)	$\log C$	$\log t$	
31.40	8	0.10	0.32	−2.4948	0.9030	$m = 1.28$
	16	0.23	0.73	−2.1366	1.2041	$K_c = 2.18 \times 10^{-4}$
	24	0.40	1.27	−1.8962	1.3802	$r = 0.9991$
	32	0.57	1.81	−1.7424	1.5051	
	40	0.78	2.48	−1.6056	1.6020	
	48	1.00	3.18	−1.4976	1.6812	

T is the temperature, R is the gas constant, A and B are constants.

By plotting a line between $\ln\ln[1/(1-\alpha)]$ or $\ln\{[1-(1-\alpha)]^{1-n}/(1-n)\}$ and $1/T$, we can caculate the decoking reaction activation energy from the slope as listed in table 5.

It has been recognized that during the cracking of C_2H_6 and C_2H_4, both slight cracking and deep cracking, coke deposition occurs, and the main coking reactions can be represented as follows:

$$
\begin{aligned}
&C_2H_6 \rightarrow 2C + 3H_2\\
&C_2H_4 \rightarrow 2C + 2H_2\\
&C_2H_4 \xrightarrow{-H_2} C_2H_2 \rightarrow 2C + H_2\\
&3C_2H_4 \xrightarrow{-3H_2} C_6H_6 \rightarrow\\
&\quad \text{multinuclear aromatic hydrocarbon} \xrightarrow{-xH_2} C
\end{aligned}
$$

Table 4
The results of measurement of coking reaction exponent (m) and coking reaction rate constant (K_c).

Catalyst	Coke (%)	m	K_c
9Fe/Si-2	24.91	0.92	7.12×10^{-3}
9Fe–9Mn/Si-2	3.18	1.28	2.18×10^{-4}

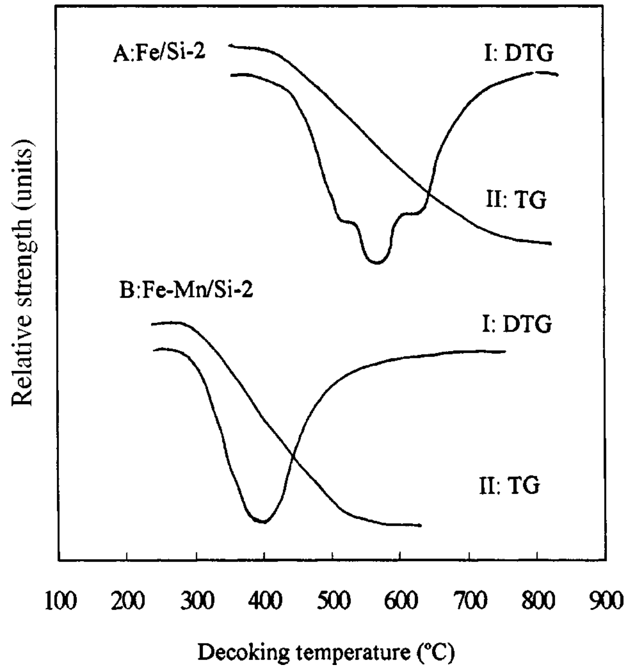

Figure 3. Decoking TG-DTG curves in air for deactivated catalyst: (A) Fe/Si-2, (B) Fe–Mn/Si-2, (I) DTG curve and (II) TG curve.

Generally, carbonaceous deposition formed from C_2H_4/C_2H_6 cracking reaction is by de-escalate H/C atom ratio. Furthermore, the carbonaceous species with lower H/C ratio will become more and more difficult to be decoked. Just the same phenomenal coking reaction does exist during the conversion of C_2H_6 with CO_2 to C_2H_4.

From figure 3, we can observe that, for Fe/Si-2, on its decoking DTG curve there are two decoking peaks, the temperatures of which are 550 and 650 °C, respectively. No doubt, the decoking peak at lower temperature indicates that the coke is more easily to be decoked than the coke at high decoking peak temperature. Accordingly the first peak at the temperature of 550 °C may correspond to the decoking of the carbonaceous deposition having low C/H ratio and the second peak at the temperature of 650 °C to decoking of the carbonaceous deposition having high C/H ratio. Generally, the decoking temperature is in the range 400–700 °C. Whereas for Fe–Mn/Si-2 on its decoking DTG curve there is only one decoking peak, the temperature of which is 400 °C. The peak may correspond to decoking of carbonaceous deposition having low C/H ratio. Its decoking temperature is in the range of 305–520 °C, as listed in table 6. The results in table 5 show that decoking reaction orders of coked Fe/Si-2 and coked Fe–Mn/Si-2 catalysts in air are 1. The decoking reaction activation energy of Fe–Mn/Si-2 is 19.97 kcal/mol lower than that of Fe/Si-2. This implies that the regeneration of deactivated Fe–Mn/Si-2 is also easier than that of deactivated Fe/Si-2. It is reasonably understood that decoking of coke on Fe–Mn/Si-2 is far easier than that on Fe/Si-2 and that Fe–Mn/Si-2 has much better performance of regeneration.

3.3.2. Regeneration performances of Fe/Si-2 and Fe–Mn/Si-2 catalysts

The catalytic performances of Fe/Si-2 and Fe–Mn/Si-2 catalysts before and after regeneration for conversion of C_2H_6 or dilute C_2H_6 in FCC off-gas with CO_2 are listed tables 7 and 8. These results show that Fe–Mn/Si-2, after regeneration can reach the fresh state, without any loss in reaction activity and C_2H_4 selectivity. While Fe/Si-2 catalyst does not have such better regeneration performance

Table 5
Calculation values of decoking reaction order (n) and decoking reaction activation energy (E) in air.

Catalyst	n	E (kcal/mol)
9Fe/Si-2	1	21.88
9Fe–9Mn/Si-2	1	19.97

Table 6
TG-DTG results of decoking in air for the coked Fe/Si-2 and Fe–Mn/Si-2 catalysts.

Catalyst	Sample weight (mg)	Coke (mg)	Decoking temperature (°C)	Decoking (mg)	Decoking (%)
9Fe/Si-2	49.70	7.80	400–700	7.75	99.3
9Fe–Mn/Si-2	43.30	5.09	305–520	4.85	95.0

Table 7
Comparison of catalytic performance of Fe/Si-2 and Fe–Mn/Si-2 catalysts at states of fresh and regeneration for conversion of C_2H_6 with CO_2 to C_2H_4.[a]

Catalyst	State	Conversion (%)		Selectivity (%)	
		CO_2	C_2H_6	CH_4	C_2H_4
Fe/Si-2	Fresh	24.7	62.1	26.0	74.0
	Regen.	20.6	57.9	30.2	69.8
Fe–Mn/Si-2	Fresh	39.1	68.6	7.7	92.3
	Regen.	37.5	66.8	7.3	92.7

[a] Reaction conditions: 800 °C, 0.1 MPa, 1000 h^{-1}, $C_2H_6/CO_2 = 1:1$, 40 h. Regeneration conditions: 600 °C, air, 4 h.

Table 8
Comparison of catalytic performance of Fe/Si-2 and Fe–Mn/Si-2 catalysts at states of fresh and regeneration for conversion of dilute C_2H_6 in FCC off-gas with CO_2 to C_2H_4.[a]

Catalyst	State	Conversion (%)		Selectivity (%)	
		CO_2	C_2H_6	CH_4	C_2H_4
Fe/Si-2	Fresh	28.3	63.5	21.9	78.1
	Regen.	23.5	57.7	27.7	72.3
Fe–Mn/Si-2	Fresh	38.6	67.6	6.6	93.4
	Regen.	37.7	66.1	6.5	93.5

[a] Reaction conditions: 800 °C, 1000 h^{-1}, C_2H_6 (in FCC off-gas) = 18.8%, $C_2H_6/CO_2 = 1:1$, 0.1 MPa, 40 h. Regeneration conditions: 600 °C, air, 4 h.

both for pure C_2H_6 and dilute C_2H_6 in FCC off-gas reaction with CO_2 to C_2H_4. Generally, Fe–Mn/Si-2 is a desirable catalyst.

4. Conclusions

(1) Fe–Mn/Si-2 catalyst exhibits desirable catalytic performance for the dehydrogenation of C_2H_6 with CO_2 as an oxidant to C_2H_4. Especially with the addition of Mn promoter onto the Fe/Si-2 catalyst, both the reaction activity and C_2H_4 selectivity were improved greatly.

(2) The coking deposition, during C_2H_6 reaction with CO_2, on Fe/Si-2 and Fe–Mn/Si-2 catalysts increases with coking reaction time on stream. Whereas, with the addition of Mn promoter onto Fe/Si-2 catalyst, the coking deposition on the catalyst is prohibited greatly. The coking deposition equation with reaction time on stream is expressed as follows:

for 9Fe/Si-2 catalyst,

$$C = 7.12 \times 10^{-3} t^{0.92};$$

for 9Fe–9Mn/Si-2 catalyst,

$$C = 2.18 \times 10^{-4} t^{1.28}.$$

(3) The decoking of deactivated Fe–Mn/Si-2 is far easier than that of Fe/Si-2. And the regeneration of Fe–Mn/Si-2 is also more facile than for the deactivated Fe/Si-2 catalyst. Fe–Mn/Si-2 has much better performance of regeneration.

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