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Article

Dehydration of bio-ethanol to ethylene over iron exchanged HZSM-5

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ABSTRACT

Iron exchanged ZSM-5 with Si/Al ratio from 25 to 300 prepared by three consecutive ion exchanges was used for the dehydration of ethanol to ethylene. The iron exchanged ZSM-5 (Si/Al = 25) catalyst with an iron content of 0.46 wt% gave 97%–99% yield of ethylene at 98%–99% conversion of ethanol at 260 °C and 0.81 h⁻¹ liquid hourly space velocity. The high performance was maintained for 60 d on-stream. X-ray diffraction, Fourier transform infrared spectroscopy of pyridine adsorption, NH₃ temperature-programmed desorption and diffuse reflectance UV-vis spectroscopy were used for catalyst characterization. Ion exchange with iron decreased the total acidity of the zeolite, especially the strong acid sites and Brønsted acid sites. The doped iron species were distributed over Fe-ZSM-5 as predominantly isolated Fe³⁺. Therefore, the catalytic performance for ethanol dehydration to ethylene was improved.

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1. Introduction

Ethylene is one of the most important chemicals with a large demand and production. The manufacture of ethylene in industry currently is by the thermal cracking of liquefied petroleum gas or naphtha [1]. This is, however, confronted with the challenges of decreasing petroleum resources and severe environmental problems. As is known, bio-ethanol is a renewable material and it is now produced on a large scale through fermentation processes [1–4]. Therefore, the catalytic conversion of ethanol offers a green route to the production of ethylene and has been paid more attention [1–14].

Currently, many catalysts have been developed for ethanol dehydration to ethylene, including oxides [11,12,15], hetero-

polyacids [8,16] and zeolites [5,17–21]. A 98.7% ethylene yield was obtained at 460 °C by a TiO₂/γ-Al₂O₃ catalyst [12]. Dogu's group [16] developed heteropolyacid catalysts for use at low reaction temperature; however, the ethylene selectivity was only 77.0% at 250 °C. Zeolites have been widely used in many fields, such as environmental decontamination, the detergent industry, and catalysis. Since the 1980s, researchers have used zeolites for the dehydration of ethanol to ethylene [1]. The zeolites used were ZSM-5, β zeolite, Si-Al-phosphate (SAPO) zeolite, A type zeolite, and AM-11 type zeolite [1]. Among these zeolite catalysts, the most promising is ZSM-5 zeolite [1,2,4,18,22–24], which has many obvious merits, such as a regular pore structure, outstanding thermal and hydrothermal stability, low formation of coke, high surface area, and adjusta-

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ble acidity [25]. Guo's group [4] studied a nano-scale HZSM-5 zeolite that gave >98.43% ethylene selectivity at >98.40% conversion at 240 °C for 630 h. Zhao's group [2] used a steam treated HZSM-5 zeolite as the catalyst for the ethanol hydration to ethylene and obtained > 90% ethylene yield at 275 °C; this excellent performance could be maintained for 350 h. Besides these, metal-modified HZSM-5 zeolite catalysts were also studied [18,24]. Le Van Mao *et al.* [24] investigated bioethanol dehydration to ethylene using a ZSM-5/Zn-Mn catalyst. The result showed that when the reaction temperature reached 400 °C, the conversion of ethanol was 96% and the selectivity to ethylene was 49%. Ouyang *et al.* [18] performed ethanol dehydration to ethylene over La-doped ZSM-5 zeolite. The stability measurement in the laboratorial bioreactor displayed that both the conversion of ethanol and selectivity to ethylene over this catalyst was maintained at >98% for >950 h at 260 °C.

Iron doped ZSM-5 was verified to be active for the transformation of ethanol into hydrocarbons [14,26–30]. The hydrocarbon product consisted of predominantly C₁–C₉ hydrocarbons, *i.e.*, alkanes, olefins and aromatics. However, in the literature, a high iron loading (up to 10 wt% [30]), ZSM-5 with a relatively high Si/Al ratio (>40 [26,31]), and high reaction temperature (up to 400 °C [27,30]) were used. As a result, in the conversion of ethanol, C₃⁺ olefins and aromatic compounds were the main products [30,31].

In this paper, the dehydration of ethanol to ethylene was carried out over an iron exchanged ZSM-5 with the Si/Al ratio ranging from 25 to 300. The iron exchanged ZSM-5 catalyst with a low Si/Al ratio exhibited a high catalytic performance for ethanol dehydration to ethylene at a low reaction temperature. The structure and properties of H-ZSM-5(25) and Fe-ZSM-5(25) catalysts were also studied.

2. Experimental

2.1. Preparation of catalysts

HZSM-5 powder (purchased from Fuxu Zeolite Corporation, China) with different molar ratios of Si/Al = 25–300 was first calcined in air at 550 °C for 4 h. Iron (Fe) exchanged ZSM-5 catalyst was obtained by three consecutive ion exchanges of HZSM-5 with aqueous solutions of iron nitrate (Fe(NO₃)₂·9H₂O). First, the calcined powder of HZSM-5 was dispersed into a 0.3 mol/L aqueous solution of metal nitrate salt using 10 mL solution per gram of zeolite. The pH of the solution was controlled at 1.5 in accordance with previous papers [26,31]. After that, the resulting mixture was magnetically stirred at 25 °C for 12 h. After filtration, rinsing and drying at 120 °C, the catalyst was calcined at 550 °C for 4 h. The as-prepared catalyst was named as Fe-ZSM-5(*X*), where *X* refers to the Si/Al molar ratio of the ZSM-5 zeolite. Before it was used in the reaction, the catalyst was pressed, crushed and sieved into the 20–30 mesh fraction. The iron content of Fe-ZSM-5(25) was determined by flame atomic absorption spectrometry (performed by a Varian AA240 apparatus). The result showed that the Fe-ZSM-5(25) catalyst possessed an iron content of 0.46 wt%.

2.2. Catalyst characterization

X-ray diffraction (XRD) was carried out with a Bruker D8-Advance X-ray diffraction equipment with Cu K_α radiation operated on 40 kV and 40 mA. The pattern was recorded over the 2θ angle ranging from 5° to 80° at a scan rate of 5°/min. NH₃ temperature-programmed desorption (NH₃-TPD) was conducted by employing a Quantachrome Autosorb-1 analyzer with a TCD. The catalyst was first heated at a rate of 10 °C/min from room temperature to 450 °C and pretreated at that temperature for 0.5 h under argon. After it was cooled to 100 °C, the catalyst was subjected to NH₃-saturation in a stream of 5% NH₃/He with a flow rate of 40 mL/min. After purging with helium at 100 °C for 0.5 h, NH₃ was desorbed by heating the catalyst to 650 °C at a rate of 15 °C/min.

Fourier transform infrared (FT-IR) spectroscopy of pyridine adsorption was recorded using a Varian 3100 spectrometer equipped with a liquid nitrogen cooled MCT detector. The resolution and scan number were 4 cm⁻¹ and 32, respectively. First, the catalyst was ground and dispersed in KBr powders (mass ratio = 33/100). Then, it was pressed into a disc and pre-heated at 400 °C for 4 h under N₂ in a Harrick *in situ* IR cell. After it was cooled to room temperature, the catalyst was exposed to pyridine vapor for 1.5 h. The catalyst was heated at 250 °C for 1.5 h in a N₂ atmosphere, followed by exposure to 0.1 MPa vacuum at room temperature for 3 h for removing gaseous and physisorbed pyridine molecules. Then the catalyst was used for the FT-IR measurement. Diffuse reflectance spectroscopy (DRS UV-VIS) was conducted by using a Perkin Elmer Lambda 35 spectrometer equipped with a 60 mm integrating sphere using BaSO₄ as standard.

2.3. Catalytic reaction

The catalytic reaction was performed in an electrically heated fixed bed reactor (*i.d.* = 10 mm, length = 400 mm). Catalyst granules (3 g) were charged into the middle of reactor. Before reaction, the temperature was raised to a preset one in the range of 200–320 °C. Bio-ethanol (60 wt% aqueous solution) was directly pumped into the reactor by a micro-pump without prior gasification or any diluent gas. The liquid hourly space velocity (LHSV) was controlled at 0.84 h⁻¹. Gaseous and liquid products from the bottom of the reactor were passed through a gas-liquid separator. The gaseous products were analyzed by a TCD gas chromatograph (PE Clarus 500) with a Porapak Q column. The liquid products were analyzed by an FID gas chromatograph (Shandong Lunan SP-2000B GC) with a SE-54 column. The conversion (denoted as *x*) and product selectivities (denoted as *S_i*) were calculated in accordance with a previous paper [20].

3. Results and discussion

3.1. Characterization of the catalysts

Fig. 1 shows the XRD patterns of HZSM-5(25) and Fe-ZSM-5(25). Both patterns present a set of diffraction peaks

Fig. 1. XRD patterns of (1) HZSM-5(25) and (2) Fe-ZSM-5(25).

at $2\theta = 7.9^\circ, 8.8^\circ, 23.0^\circ, 23.2^\circ, 23.6^\circ, 23.9^\circ$ and 24.4° , indicating that these two catalysts possess the same ZSM-5 zeolite structure. For the Fe-ZSM-5 catalyst, besides the peaks assigned to ZSM-5, no other peak was observed. These observations showed that the ion exchange process neither deteriorated the crystal structure of ZSM-5 zeolite nor generated a new phase detectable by XRD.

Fig. 2 shows the FT-IR spectra of pyridine adsorption on HZSM-5(25) and Fe-ZSM-5(25). Bands at 1540 and 1450 cm^{-1} were present. These can be assigned to Brönsted and Lewis acid sites, respectively [32]. One can see that both the bands for the Brönsted and Lewis acid sites showed changes in their integrated areas with the catalyst, indicating variations in the concentrations of the Brönsted and Lewis acid sites. The ratio of the integrated areas of the bands at 1540 and 1445 cm^{-1} can be employed to evaluate the relative concentration of Brönsted and Lewis acid sites [33]. These ratios, denoted as B/L, for the different catalysts are summarized in Table 1. One can see that the Fe-ZSM-5(25) catalyst has an obviously lower B/L value than the HZSM-5(25) zeolite.

Fig. 3 shows the NH_3 -TPD profiles of HZSM-5(25) and Fe-ZSM-5(25). The peaks in these desorption profiles can be classified into two groups, low-temperature peaks (LT; < 300

Fig. 2. FT-IR of pyridine adsorption of (1) HZSM-5(25) and (2) Fe-ZSM-5(25).

Table 1

Acidity and acid site amounts of the catalysts determined by NH_3 -TPD.

Catalyst	LT		HT		ΣC	C_H/C_L	B/L
	C_L (mmol/g)	$T_{m,L}$ (°C)	C_H (mmol/g)	$T_{m,H}$ (°C)			
HZSM-5(25)	0.147	202	0.102	469	0.249	0.70	1.42
Fe-ZSM-5(25)	0.121	215	0.038	438	0.159	0.29	0.25

Notes: C and T_m refer to the concentration of acid sites and temperature of the desorption peak at its maximum; ΣC refers to the total acidity; C_H/C_L is the area ratio of HT acid sites to LT acid sites; B/L is the concentration rate of Brönsted to Lewis acid sites determined by FT-IR of pyridine adsorption.

°C) and high-temperature ones (HT; > 300 °C). The concentration of acid sites (C) and temperature for the maximum of the peaks (T_m) are listed in Table 1. The distribution of acid sites was also calculated from the TPD profiles by the deconvolution method. The ratios of the concentration of HT acid sites to LT acid sites, denoted as C_H/C_L , were also calculated. HZSM-5(25) exhibited a LT peak at 202 °C and a HT peak at 469 °C, suggesting that two types of acid sites were present. Fe-ZSM-5 showed a clear decrease in the total acidity relative to the pristine HZSM-5 zeolite. Compared to HZSM-5(25), for Fe-ZSM-5(25), the LT peak increased to the higher temperature at 215 °C. However, the HT peak decreased to a lower temperature (438 °C).

Fig. 4 shows the UV-VIS spectra of HZSM-5(25) and Fe-ZSM-5(25). The electronic spectrum in the UV-visible region is a useful technique for studying the electronic state of isolated transition metal ions. According to the literature [34,35], the UV/VIS spectrum is especially sensitive to the charge transfer bands of the iron ion. The wavelength of the bands reflects the coordination number and the degree of aggregation. One can see that HZSM-5(25) showed a strong band at 240 nm, which is related to the Al units of the T_1 transition charge transfer processes [36]. In comparison, Fe-ZSM-5(25) exhibited three characteristic absorptions at 232, 277, and 357 nm. In Brückner's work [34], the bands below 300 nm were ascribed to isolated Fe^{3+} sites. Their position depends on the number of ligands. In the present work, the band at 232 nm was attributed to isomorphously incorporated Fe^{3+} ions in the zeolite framework

Fig. 3. NH_3 -TPD profiles of (1) HZSM-5(25) and (2) Fe-ZSM-5(25).

Fig. 4. DRS UV-VIS spectra of (1) HZSM-5(25) and (2) Fe-ZSM-5(25).

with tetrahedral or higher coordination [34,36], and the band at 277 nm to isolated extraframework Fe^{3+} sites in octahedral coordination [37]. Thus, we concluded that framework and extraframework Fe^{3+} were present simultaneously in Fe-ZSM-5(25). The small band at 357 nm was associated with the iron ions of small oligomeric Fe_xO_y clusters [34,38]. There was hardly any band that can be attributed to large Fe_2O_3 particles, which would show bands above 450 nm [34,35], observed. These results suggested that the Fe species was distributed over the Fe-ZSM-5 catalyst predominantly as isolated

framework and extraframework Fe^{3+} , and a small amount of oligomeric Fe_xO_y clusters. However, hardly any large Fe_2O_3 particles existed.

3.2. Dehydration of ethanol to ethylene over the catalysts

The Si/Al ratio of the zeolites remarkably affected the distribution and strength of the surface acid sites which played a vital role in the dehydration of ethanol to ethylene [10]. Fig. 5(a) shows the dehydration of ethanol to ethylene over HZSM-5(*X*) as a function of the *X* (Si/Al ratio) value. The reaction temperature was 230 °C. One can see that the conversion of ethanol increased first, and reached a maximum (79.2%) at the Si/Al ratio of 100, and then it decreased with the further increase of the Si/Al ratio value. However, the yield of ethylene decreased monotonically with the Si/Al ratio. HZSM-5(25) zeolite gave the highest yield of ethylene (47%).

Fig. 5(b) shows the ethanol dehydration to ethylene over Fe-ZSM-5(*X*) as a function of the *X* (Si/Al ratio) value at 230 °C. The results showed that both the conversion of ethanol and yield of ethylene decreased uniformly with increasing Si/Al ratio. As a result, the highest yield of ethylene (84%) was obtained at the Si/Al ratio of 25.

Fig. 5(c) shows the effect of reaction temperature on the dehydration of ethanol to ethylene over Fe-ZSM-5(25). When the reaction temperature increased, the conversion of ethanol increased from 53.3% (at 200 °C) to above 99.8% (above 260

Fig. 5. Effect of Si/Al ratio on the dehydration of ethanol to ethylene over (a) HZSM-5(*X*) and (b) Fe-ZSM-5(*X*) at reaction temperature = 230 °C and LHSV = 0.81 h⁻¹; (c) Effect of reaction temperature on the dehydration of ethanol to ethylene over Fe-ZSM-5(25) at LHSV = 0.81 h⁻¹; (d) Conversion of ethanol and yield of ethylene as a function of time-on-stream over HZSM-5(25) and Fe-ZSM-5(25) at reaction temperature = 260 °C and LHSV = 0.81 h⁻¹.

°C), indicating that this reaction is accelerated by increasing the reaction temperature. However, the yield of ethylene increased first from 47.8% (at 200 °C) to 98.5% (at 260 °C) and then it decreased with further increase in reaction temperature. The highest ethylene yield (98.5%) was obtained at the reaction temperature of 260 °C.

Fig. 5(d) shows the effect of time-on-stream on ethanol dehydration to ethylene over HZSM-5(25) and Fe-ZSM-5(25). At 260 °C reaction temperature and 0.81 h⁻¹ of LHSV, >70% of ethylene yield at >95% ethanol conversion was obtained over HZSM-5(25), which was maintained for about 70 h. Comparatively, at the same reaction conditions, the better catalytic performance (>97% ethylene yield at > 98% ethanol conversion) was obtained over Fe-ZSM-5(25). The high catalytic activity was maintained for as long as 1440 h. The outstanding stability of Fe-ZSM-5(25) indicated a very promising potential for further development.

Table 2 shows the detailed results of the conversion of ethanol over the various catalysts. According to previous work [6,9,39,40], the catalytic activity for ethanol dehydration is correlated with the acid centers of the catalysts [6]. As is known, the surface acidity of a zeolite is associated with the Si/Al ratio of zeolite. HZSM-5(25) provided a larger acid concentration than HZSM-5(300) due to the lower Si/Al ratio [41]. One can see that HZSM-5(25) (Entry 1) exhibited a similar conversion of ethanol to HZSM-5(300) (Entry 2). However, the former catalyst produced large numbers of C³⁺ hydrocarbons, while the latter one only gave ethylene (C₂H₄) and diethyl ether ((C₂H₅)₂O). Takahara *et al.* [39] studied the dehydration of ethanol over various solid acid catalysts and suggested that diethyl ether is the reaction intermediate for the formation of ethylene. This was supported by Domen *et al.* [10] using FT-IR. Inaba *et al.* [21,30] and Calsavara *et al.* [31] studied the conversion of ethanol to hydrocarbons [21,30,31] and proposed that ethanol first dehydrates to generate ethylene, which was further transformed to higher hydrocarbons and aromatics. Therefore, for HZSM-5(300), the low surface acidity led to the formation of diethyl ether as a reaction intermediate. However, for HZSM-5(25), the high surface acidity resulted in the further transformation of ethylene to C³⁺ hydrocarbons as byproducts.

One can see in Table 2 that after ion exchange, Fe-HZSM-5(25) (Entry 3) exhibited a higher yield of ethylene (98.52%) than HZSM-5(25) (73.30%). This would be due to the modification of the acidity of HZSM-5. According to Aguayo *et al.* [40], for the conversion of ethanol to hydrocarbons, the de-

hydration of ethanol to ethylene occurs over weak acid sites, whereas the subsequent reaction steps which generate the higher hydrocarbons and aromatics require sites of a higher acid strength. The NH₃-TPD results (Fig. 3 and Table 1) displayed that the ion exchange of iron decreased the total acidity of ZSM-5 zeolite, especially the HT acid sites. As a result, the C_H/C_L value of Fe-ZSM-5(25) (0.29) was lower than that of HZSM-5(25) (0.7). Therefore, it is reasonable that the significant reduction of the HT acid sites of HZSM-5 by the ion exchange of iron benefited ethanol dehydration to ethylene.

One can also see in Table 2 that a relatively low reaction temperature (230 °C, Entry 4) is propitious for the formation of the reaction intermediate diethyl ether through inter-molecular dehydration [12]. However, a relatively high reaction temperature (290 °C, Entry 5) led to the further transformation of ethylene to C³⁺ hydrocarbons. Besides, the influence of LHSV on the catalytic performance was also studied. At 230 °C, 64.70% ethylene selectivity and 33.37% diethyl ether selectivity at 98.99% ethanol conversion was obtained at LHSV = 0.47 h⁻¹ (Entry 4). However, with the increase of the LHSV (Entries 6–8), the conversion of ethanol and selectivity to ethylene decreased while the selectivity to diethyl ether increased. This can be explicated by the fact that the contact time of ethanol molecules with the zeolite catalyst was shortened with the increase of LHSV, which resulted in the incomplete reaction of ethanol and led to the formation of the reaction intermediate diethyl ether [18].

Phillipes *et al.* [6] studied ethanol dehydration to ethylene on HZSM-5 zeolite. They found that although the Brönsted acid sites on HZSM-5 have high activity for ethanol conversion, these sites also can oligomerize ethylene to produce carbonaceous species, which rapidly cover the active sites and led to a dramatic reduction of HZSM-5 activity. Therefore, when used for ethanol dehydration to ethylene, the catalyst lifetime of a pristine HZSM-5 zeolite is usually short (below 60 h) [6]. In the present work, from the FT-IR of pyridine adsorption (Fig. 2), we can see that the B/L value of Fe-ZSM-5(25) was obvious lower than that of HZSM-5(25) (the former was 0.25, and the latter was 1.42). We also can see that in Fig. 5(d), Fe-ZSM-5(25) exhibited a lifetime as long as 1440 h time-on-steam, which was obvious longer than the pristine HZSM-5(25) zeolite [4,6,39]. It was reasoned that the decrease of the amount of Brönsted acid sites on HZSM-5 by the ion exchange of iron helped increase the catalyst lifetime due to the decrease of the generation of carbonaceous species catalyzed by the Brönsted

Table 2
Catalytic reaction of ethanol over the catalysts.

Entry	Sample	<i>t</i> /°C	LHSV (h ⁻¹)	Conversion of ethanol (%)	Selectivity (%)						Yield of ethylene (%)
					C ₂ H ₄	(C ₂ H ₅) ₂ O	C ₂ H ₆ and C ₃	C ₄	C ₅	C ₆₊	
1	HZSM-5(25)	260	0.47	96.80	75.71	0	10.27	8.87	4.73	0.41	73.30
2	HZSM-5(300)	260	0.47	96.76	41.41	58.59	0	0	0	0	40.07
3	Fe-ZSM-5(25)	260	0.47	99.74	98.78	0	0.99	0.07	0.16	0	98.52
4	Fe-ZSM-5(25)	230	0.47	98.99	64.70	33.37	0.88	1.03	0	0	64.04
5	Fe-ZSM-5(25)	290	0.47	99.99	43.82	0	11.65	7.57	11.37	25.6	43.82
6	Fe-ZSM-5(25)	230	0.94	71.57	58.33	41.47	0	0	0	0	41.75
7	Fe-ZSM-5(25)	230	1.88	64.93	42.53	57.45	0	0	0	0	27.61
8	Fe-ZSM-5(25)	230	3.79	55.97	38.19	71.77	0	0	0	0	21.37

acid sites of the zeolite.

In this work, we prepared the Fe-ZSM-5 catalyst by a method of three consecutive ion exchanges. As is known, the ion exchange method is usually employed to prepare a catalyst with a high dispersion of the metal component [42]. In Fig. 4, it was found that the Fe species was distributed over the Fe-ZSM-5 as predominantly isolated framework and extraframework Fe^{3+} , and a small amount of oligomeric Fe_xO_y clusters. However, hardly any large Fe_2O_3 particles were detected. Guan *et al.* [37] studied the dehydration of ethanol to ethylene over FeSBA-15 synthesized by a direct synthesis method, and showed results that suggested that isolated Fe^{3+} species serve as the active sites for the formation of ethylene, whereas FeO_x clusters catalyzed the formation of ethylene and especially aldehyde. Therefore, in this work, the good catalytic performance of Fe-ZSM-5(25) was attributable to the large amounts of isolated framework and extraframework Fe^{3+} species and the low concentration of FeO_x clusters and Fe_2O_3 particles on the catalyst.

4. Conclusions

Iron exchanged ZSM-5 zeolite catalysts with Si/Al molar ratio ranging from 25 to 300 were used for ethanol dehydration to ethylene. Fe-ZSM-5 with a Si/Al ratio equal to 25 showed the best catalytic performance. At 260 °C and 0.81 h⁻¹ of LHSV, 97%–99% yield of ethylene at 98%–99% conversion of ethanol was obtained, which was maintained for 1440 h of time-on-stream. These catalysts were characterized by XRD, NH_3 -TPD, FT-IR of pyridine adsorption and DRS UV-VIS. The results suggested that (1) ion exchange neither deteriorated the crystal structure of HZSM-5 zeolite nor generated a new phase detectable by XRD, (2) the ion exchange of iron significantly decreased the strong acid sites of the zeolite, which benefited ethanol dehydration to ethylene, (3) the ion exchange of iron decreased the Brønsted acid sites of the zeolite, which helped extend the catalyst lifetime due to the decrease of the generation of carbonaceous species catalyzed by the Brønsted acid sites of the zeolite, and (4) the doped Fe species on the

Fe-ZSM-5 was in the form of predominantly framework and extraframework Fe^{3+} , which increased the catalytic activity of the catalyst for ethanol dehydration to ethylene.

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Graphical Abstract

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A Fe-ZSM-5(25) zeolite catalyst showed excellent activity for ethanol dehydration to ethylene. A 97%–99% yield of ethylene at 98%–99% conversion of ethanol was achieved.

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生物质乙醇在 Fe-HZSM-5 分子筛催化剂上脱水制乙烯

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摘要: 乙烯是一种重要的大宗化工原料。目前国内外乙烯的生产方法主要是石脑油裂解法。但是, 随着全球性石油资源供求关系日趋紧张, 以及该生产过程存在较大环境污染, 该工艺面临严峻挑战。生物乙醇是一种可以通过生物质发酵获得的可再生资源。因此, 生物质乙醇催化脱水制乙烯工艺受到越来越多研究者关注。该技术的关键在于高性能乙醇脱水制乙烯催化剂的开发。研究发现, Si/Al 比大于 40 的 Fe 改性 ZSM-5 分子筛在乙醇转换制碳氢化合物的催化反应中具有较高活性, 当反应温度大于 400 °C 时, 可生成 C₁–C₉ 的烷烃、烯烃和芳香烃, 其中以 C₃ 产物和芳香烃产物为主。本文研究了 Si/Al 比为 25–300 的 Fe 离子交换 ZSM-5 分子筛在乙醇脱水制乙烯反应中的催化活性, 并利用 XRD, NH₃-TPD, 吡啶吸附 FT-IR 和 DRS UV-VIS 等表征手段, 研究了催化剂的晶相结构、表面组成及酸性位点等, 进而探究了该催化反应的反应机理。

我们首先考察了 Si/Al 比为 25–300 的 HZSM-5 分子筛。随着分子筛 Si/Al 比增大, 乙醇转化率先增加后降低, 在 Si/Al 比为 100 时获得最高值; 但是乙烯收率随着 Si/Al 比的增加而持续下降, Si/Al 比为 25 时有其最高值 47%。经产物分析, HZSM-5(25) 和 HZSM-5(300) 虽具有相似的乙醇转化率, 但前者产生大量 C₃₊ 产物, 而后者产物只有乙烯和乙醚。据文献报道, 乙醚是乙醇脱水制乙烯的中间产物, 它的进一步脱水产生乙烯, 而乙烯可进一步转化生成 C₃₊ 产物。因此, 由于 HZSM-5(300) 表面酸性较弱, 主要生成反应中间体, 而 HZSM-5(25) 较强的表面酸性又导致乙烯进一步转化, 生成 C₃₊ 产物。然后我们考察了经过 3 次离子交换处理的 Fe-ZSM-5 催化剂。随着 Si/Al 比上升 (25–300), 乙醇转化率和乙烯收率下降, Si/Al 比为 25 时为其最高值; 随着反应温度上升, 乙醇转化率在 260 °C 时达到近 100%, 之后维持不变, 乙烯收率也在 260 °C 时为其峰值, 温度继续上升造成乙烯收率再次下降; 催化剂空速增大降低乙醇转化率和乙烯收率。经产物分析, 温度较低和空速较大时产生大量的反应中间体乙醚, 而温度较高时导致乙烯进一步转化生成 C₃₊ 产物。在反应温度为 260 °C、空速为 0.81 h⁻¹ 时, Fe-HZSM-5(25) 催化剂上乙醇转化率为 98%–99%、乙烯收率为 97%–99%, 并可实现长达 1440 h 的单程使用寿命, 该值是 HZSM-5(25) 催化剂的 20 余倍, 具有很好的工业应用前景。

为探究 Fe-ZSM-5(25) 催化剂高催化活性和长催化寿命的原因, 我们表征了催化剂。从 XRD 结果可以看出, 离子交换没有损坏 HZSM-5 的晶体结构, 也没有新的可检测到的物相产生。从 NH₃-TPD 结果看, HZSM-5(25) 的 C_H/C_L (强酸/弱酸) 比为 0.7, Fe-ZSM-5(25) 的 C_H/C_L 比为 0.29, 可知 Fe 离子交换降低了分子筛的表面酸性, 特别是强酸性位。从吡啶吸附 FT-IR 结果看, HZSM-5(25) 的 B/L (Brönsted 酸性位/Lewis 酸性位) 比为 1.42, Fe-ZSM-5(25) 的 B/L 比为 0.25, 可知 Fe 离子交换主要减少的是分子筛表面的 Brönsted 酸性位。文献报道, 乙醇脱水制乙烯主要发生在弱酸性位上, 而乙烯进一步转化为 C₃₊ 产物发生在强酸性位上。所以, 催化剂上强酸性位的减少有利于乙烯的生成反应。另据文献报道, Brönsted 酸性位是乙烯聚合、迅速覆盖催化活性位点产生积炭的催化活性中心。因此, Brönsted 酸性的降低可认为是 Fe-HZSM-5(25) 催化剂单程使用寿命较长 HZSM-5(25) 分子筛显著延长的原因。从 UV-VIS 结果得知, Fe-ZSM-5 上的 Fe 物种主要以骨架内和骨架外 Fe³⁺ 为主, 此外含有少量低聚合的 Fe_xO_y, 但几乎没有 Fe₂O₃ 颗粒存在。文献记载, Fe³⁺ 物种是乙烯形成的活性物种,

而 FeO_x 催化产生乙烯和乙醛. 因此, 催化剂中大量骨架内和骨架外 Fe^{3+} 物种的存在也可认为是该催化剂具有较强乙醇脱水制乙烯催化活性的原因之一.

关键词: 铁; ZSM-5; 脱水; 乙醇; 乙烯

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