



Remarkably enhanced stability of HZSM-5 zeolite co-modified with alkaline and phosphorous for the selective conversion of bio-ethanol to propylene



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ABSTRACT

The effects of alkaline, phosphorous and dual alkaline-phosphorous modifications on the selective conversion of bio-ethanol to propylene over HZSM-5 zeolite catalysts were investigated. The results demonstrate that the doubly modified HZSM-5 zeolite catalyst offers higher propylene selectivity and remarkably improved catalytic stability than the parent and singly modified counterparts, which can be contributed to the formation of new mesoporous and decreased amount of strong acid sites induced by the alkaline treatment and phosphorous modification, respectively. The deactivation of the phosphorous and dual alkaline-phosphorous modified HZSM-5 zeolite catalysts was caused by carbon deposition but not by dealumination, which can be attributed to the enhanced hydrothermal stability of the framework aluminum by the modification of ZSM-5 zeolite with phosphorous.

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1. Introduction

Propylene serves as an essential feedstock for the production of polypropylene, acrylonitrile, propene oxide and many other commodity chemicals. Presently, propylene is mainly produced as a byproduct of ethylene via steam cracking of naphtha. Nevertheless, the demand for propylene is growing faster than that for ethylene because of higher need for propylene derivatives such as polypropylene and propylene oxide. Therefore, it is very important to develop other routes for propylene production [1–3]. From the perspective of increasing oil prices and environmental protection, selective conversion of ethanol to propylene (ETP) has attracted much attention in recent years because ethanol can be obtained in large scale by fermentation of biomass [4–20].

Among the numerous catalysts reported for the ETP reaction, HZSM-5 zeolite is the most widely used due to its unique characteristics, such as intrinsic acidity, high surface area and well manageable pore sizes [4–15]. However, the purely microporous nature of zeolites frequently poses transport limitations, which usually deactivates the zeolite catalyst quickly [21]. To improve the catalyst effectiveness, the diffusion rate can be enhanced by introducing the additional mesopores in microporous zeolite par-

ticles [22]. The desilication method with alkaline solutions has been widely used in recent years for the creation of intracrystalline mesoporosity in ZSM-5 zeolites due to its simplicity and high efficiency [23]. Unfortunately, the strengthened acidity of the HZSM-5 zeolite due to the desilication induced by alkaline treatment is expected to reduce propylene selectivity and to increase carbon deposition rate. Therefore, it is highly desirable to modify the acidity of the alkaline modified HZSM-5 zeolite. As well known, phosphorous modification is a very effective way to control the zeolite acidity. Furthermore, the hydrothermal stability of zeolite could be improved by phosphorous modification [6,10,11], which is very important for the ETP reaction [5,6,9].

To the best of our knowledge, there has been no report on the HZSM-5 zeolites modified by both alkaline treatment and phosphorous as catalysts in the selective dehydration of ethanol into propylene. On the other hand, all of the former studies use the mixture of vaporized ethanol and N₂ as feedstock [4–20]. However, bio-ethanol is produced by fermentation in water, and the separation of water by distillation to >92% ethanol is costly [24]. If ethanol with concentration <92% could be used, the ETP process will be much more cost-effective. Therefore, in this work, the effects of alkaline treatment and phosphorous modification on the catalytic performance of the HZSM-5 zeolite for the selective conversion of bio-ethanol into propylene were systematically studied for the first time. Based on the results, the higher propylene selectivity and especially the remarkably enhanced catalyst stability

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were obtained by the combined modifications with alkaline and phosphorous.

2. Experimental

2.1. Catalyst preparation

The HZSM-5 zeolite (HZ, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 69$, molar) and NaOH solution (0.4 mol/L) at a mass ratio of 1:20 were heated to 60 °C with stirring in the Teflon-lined stainless-steel autoclave. After processing for 2 h, the reactor cooled rapidly in cold water. Then, the zeolite was recovered after several cycles of centrifuging and washing with deionized water, dried overnight at 110 °C and calcined in air at 550 °C for 6 h. The obtained ZSM-5 was turned into the H-form by three consecutive ion-exchanges in a large excess of aqueous 1 mol/L solution of NH_4NO_3 at 85 °C and calcining again at 550 °C for 6 h, which was named as D-HZ. The HZ and D-HZ zeolites were immersed in 2 wt% H_3PO_4 solution at a mass ratio of 1:20 and continuously stirred at room temperature for 2 h and centrifuged, followed by drying at 120 °C overnight, and then calcined at 550 °C for 6 h, which were named as HZ-P and D-HZ-P, respectively.

2.2. Catalyst characterization

X-ray diffraction (XRD) measurements were undertaken using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) on a Rigaku C/max-2500 diffractometer at 40 kV and 40 mA. The patterns were recorded in the 2θ range from 5° to 50° at a scanning rate of 4/min.

^{27}Al Magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded at a spinning speed of 15 kHz on a Bruker AVANCE III 600 NMR spectrometer equipped with a 4 mm probe head and 4 mm ZrO_2 rotors at 156.4 MHz. The spectra were obtained with 0.5- μs pulses, a 1-s recycle delay and 3000 scans. The chemical shift of ^{27}Al was referenced to 1 M aqueous solution of $\text{Al}(\text{NO}_3)_3$.

Si/Al molar ratio of the sample was determined by the energy-dispersive X-ray spectrometer (EDX), via the X Flash Detector 4010 (Bruker ALX) instrument.

Nitrogen adsorption/desorption isotherms at -196 °C were obtained after outgassing the sample under vacuum at 200 °C for 12 h, using a Micromeritics ASAP2020 M + C adsorption apparatus. The total surface areas, micropore volumes and mesopore size distribution were determined by BET method, t-plot method, and BJH model, respectively.

Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out on a conventional flow apparatus equipped with a thermal conductivity detector (TCD). The sample (0.1 g) was pre-treated at 500 °C in N_2 flow (60 mL/min) for 1 h and then cooled down to 30 °C. Afterwards, NH_3 (10 vol.% in N_2 , 25 mL/min) was adsorbed at 30 °C for 30 min. Subsequently, the physically adsorbed NH_3 was removed in flow of pure N_2 at 100 °C for 1 h. Desorption of ammonia was monitored in the range of 100–550 °C using a heating rate of 10 °C/min.

Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-60H machine as the temperature increased from 30 to 850 °C under flowing air at a rate of 25 mL/min and a constant ramping rate of 10 °C/min. The coke content of the spent catalyst was determined according to weight loss between 400 and 700 °C.

2.3. Activity measurements

Catalytic reaction tests were conducted at 500 °C under atmospheric pressure in a conventional continuous flow fixed-bed reactor made of stainless steel (inner diameter 6 mm, effective length 20 cm). The catalyst (0.3 g) was placed in the center zone of the reactor. Prior to the catalytic measurements, the fresh catalyst

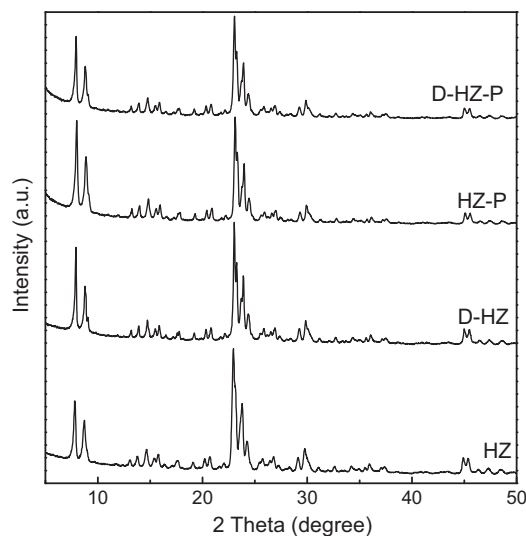


Fig. 1. XRD patterns of the parent and modified HZSM-5 catalysts.

was activated at 500 °C for 1 h in N_2 flow. Ethanol-water mixture (90 vol.% ethanol) was pumped through a piston pump (WHSV of ethanol was 3.3 h^{-1}). A gas chromatograph (Agilent 6820) equipped with a flame ionization detector (FID) was used to analyze the effluent products. The analysis process was carried out in a HP-Plot-Q capillary column with N_2 as a carrier gas. To avoid possible condensation of heavier hydrocarbons, the temperature of the effluent line was constantly maintained at 180 °C.

The conversion of ethanol and selectivity of products were determined with an accuracy of 5%. They are defined as follows:

$$\text{Conversion of ethanol\%} = (\text{n}_{\text{EtOH}(\text{in})} - \text{n}_{\text{EtOH}(\text{out})}) / \text{n}_{\text{EtOH}(\text{in})} \times 100$$

Selectivity of product $i\%$ = $(v_i C_i / \sum v_i C_i) \times 100$, where v_i and C_i are the carbon number and molar concentration of the i th product, respectively.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns for the parent and modified HZSM-5 catalysts (Fig. 1) confirmed that the MFI structure of the HZSM-5 zeolite maintained well for all the modified catalysts. It suggests that modification by NaOH and H_3PO_4 solution had no noticeable effect on the basic phase structure of the HZSM-5 zeolite. However, it was seen that both the D-HZ and HZ-P catalysts exhibited slightly lower crystallinity indicated by a decrease in the intensity of peaks at $2\theta = 23\text{--}25^\circ$. This was mainly attributed to the desilication owing to alkali treatment [25,26], and the dealumination during the alkali [25–28] and phosphoric [29] modification process, respectively. As expected, the lowest crystallinity was observed for the D-HZ-P sample because of the removal of more silicon and aluminum in the combined modifications with alkali and phosphorous.

As shown in Fig. 2, the ^{27}Al MAS NMR spectra of all the samples demonstrate two signals at 54 ppm and 0 ppm, which are originated from the tetrahedral framework aluminum and the small amount of octahedral extra-framework aluminum, respectively. For the D-HZ sample, the intensity of the band at 54 ppm decreased, while that of the band at 0 ppm increased compared with the parent HZ sample. This phenomenon was mainly contributed to the dealumination from framework accompanied with the desilication of zeolite during the alkali treatment process [25–28]. For the HZ-P

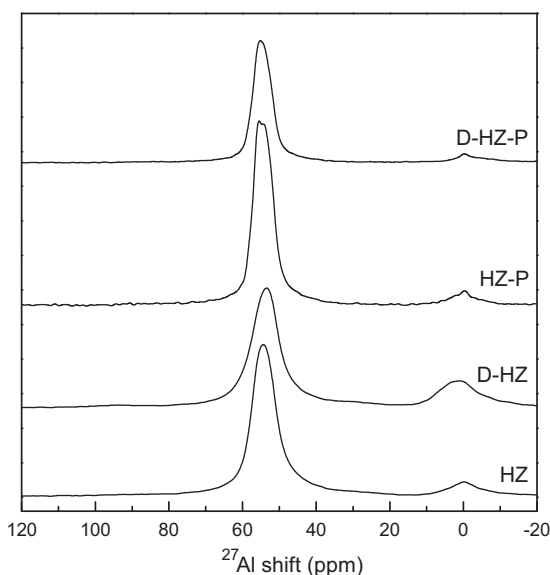


Fig. 2. ^{27}Al MAS NMR spectra for the parent and modified HZSM-5 catalysts.

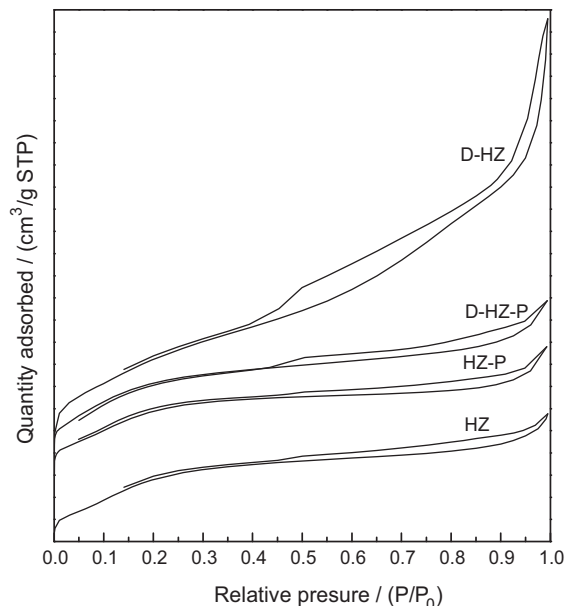


Fig. 3. N_2 adsorption/desorption isotherms of the parent and modified HZSM-5 catalysts (The curves were shifted vertically for the sake of clarity).

and D-HZ-P samples, the intensity of the band at 54 ppm had little change, since the dealumination of HZSM-5 zeolite with a high Si/Al ratio was not easy to take place during the P modification [30]. However, the intensity of the band at 0 ppm decreased noticeably, indicating that the non-framework aluminum was washed away during the phosphoric acid treatment.

The N_2 adsorption/desorption isotherms for all the catalysts are presented in Fig. 3. The hysteresis loop at $p/p_0 > 0.45$ identified for the parent HZSM-5 results from the intercrystalline mesopores of zeolite nanocrystals aggregate [31]. Compared with the parent HZSM-5, the HZ-P sample exhibits essentially the same isotherm; however, the isotherm of the D-HZ presents an obviously enhanced uptake at higher pressure and a significantly enlarged hysteresis loop, indicating the formation of large amounts of new mesopores due to desilication [32]. The modification of P results in the distinct decrease in both the uptake at higher pressure and hysteresis loop of the D-HZ sample.

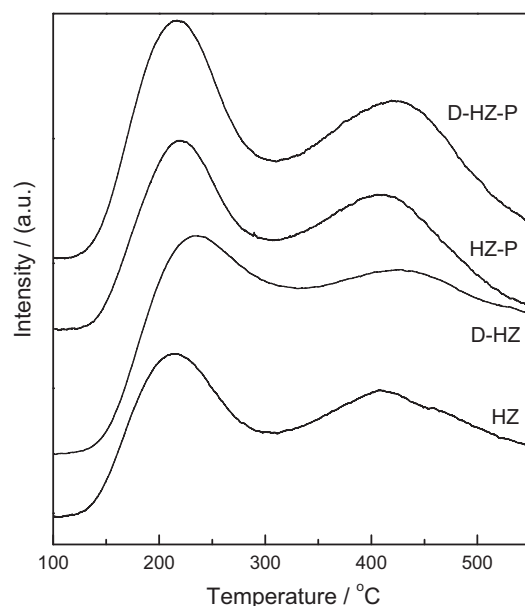


Fig. 4. NH_3 -TPD profiles of the parent and modified HZSM-5 catalysts.

The textural properties of all the samples are listed in Table 1. It can be seen that the modification of HZSM-5 with P led to a decrease in the external surface area and hence in the BET surface area. The external surface area, mesopore volume, and pore size of the D-HZ sample increased apparently, while the micropore surface area and micropore volume have been little affected. This result is in line with those obtained by other researchers [25,33]. The P modification after alkali-treatment results in remarkable decrease in the external surface area, mesopore volume, and pore size of the D-HZ sample, which was likely due to the reduction of pore dimensions or partial pore blockage by the phosphorous species introduced during the phosphoric acid treatment [34].

The values of Si/Al ratio for the parent and modified zeolites obtained from EDX measurements are also presented in Table 1. As a result of the selective silicon extraction, the Si/Al ratio of HZ decreased after the alkali-treatment. However, after modification with P, the Si/Al ratios of the HZ and D-HZ catalysts increased slightly due to the removal of the non-framework aluminum during the phosphoric acid treatment as evidenced by the above Al MAS NMR characterization.

The NH_3 -TPD profiles of the parent and modified HZSM-5 catalysts are illustrated in Fig. 4. As seen, all the catalysts showed a typical NH_3 -TPD spectrum with two maximum peaks below and above 300°C , corresponding to weak and strong acid sites, respectively. The quantitative data of NH_3 desorbed from different catalysts are listed in Table 2. Compared with the sample HZ, both the weak and strong acid sites of the D-HZ catalyst were significantly increased. This was associated with the relative higher Al content derived from desilication [33], which was evidenced by the decreasing of Si/Al ratios as seen in Table 1. After modification of HZ and D-HZ with P, the intensity of the high temperature peak decreased drastically, while that of the low temperature peak showed no evident change. The result indicates that the amount of strong acid sites of HZ and D-HZ was reduced greatly by modification with P [12]. As a result, the total amounts of acid sites of HZ and D-HZ decreased after P modification.

3.2. Catalytic performance

Fig. 5 shows the time course of the selectivity to light (C_2 – C_4) olefins and aromatics during the selective conversion of bio-

Table 1
Textural properties of the parent and modified HZSM-5 catalysts.

Sample	BET Surface area (m ² g ⁻¹)			Pore volume (cm ³ g ⁻¹)			Average pore diameter (nm)	Si/Al molar ratios
	Total	Micropore	External	Total	Mesopore	Micropore		
HZ	375	205	170	0.22	0.09	0.13	2.3	24.2
D-HZ	407	184	223	0.46	0.33	0.13	4.1	22.4
HZ-P	345	209	136	0.25	0.11	0.14	2.5	26.6
D-HZ-P	307	178	129	0.25	0.13	0.12	2.7	23.6

Table 2
NH₃-TPD results of the parent and modified HZSM-5 catalysts.

Catalyst	Area of weak acid sites (a.u.)	Area of strong acid sites (a.u.)	Area of total acid sites (a.u.)
HZ	146.6	202.0	348.6
D-HZ	198.3	335.8	534.1
HZ-P	156.1	183.6	339.7
D-HZ-P	201.5	223.4	424.9

Table 3
Comparison of performance of different modified HZSM-5 zeolite catalysts.

Catalyst	Reaction conditions	Catalytic performance	Reference
P modified HZSM-5 with SiO ₂ /Al ₂ O ₃ = 80	0.3 g, 30 mL/min, P _{EIOH} = 50 kPa, T = 550 °C	The initial selectivity of propylene was 32% and can maintain for 6 h	[6]
La modified HZSM-5 with SiO ₂ /Al ₂ O ₃ = 280	V _{EIOH} = 56%, V _{N₂} = 44%, WHSV = 0.63 h ⁻¹ , T = 550 °C	The selectivity of propylene at TOS = 8.2 h was 31% and decreased to 24% at TOS = 28.2 h	[7]
P modified HZSM-5 with SiO ₂ /Al ₂ O ₃ = 80	diluted ethanol (50% in N ₂), W/F = 1.0 × 10 ⁻² g/cm ³ min, T = 550 °C	The initial selectivity of propylene was 30.5% and decreased to 20% after 100 h	[11]
La and P co-modified HZSM-5(Ga)	diluted ethanol (50% in N ₂), W/F = 0.02 g _{cat} /mL/min, 500 °C	The initial selectivity of propylene was 28.7% and decreased to ca. 26% after 8 h	[13]
SiO ₂ modified nano HZSM-5 with size of 28 nm	diluted ethanol (50% in N ₂), WHSV = 8 h ⁻¹ , 400 °C	The initial selectivity of propylene was ca. 22% and decreased to <20% after 15 h	[14]
NaOH and P co-modified HZSM-5	90 vol% ethanol aqueous solution, WHSV = 3.3 h ⁻¹ , T = 500 °C	The selectivity of propylene at TOS = 100 h was 23%	This work

ethanol to propylene over the parent and modified HZSM-5 catalysts. Although the conversion of ethanol remains complete during the whole operation for all the samples, the selectivity of products was very different among them.

As shown in Fig. 5a, compared with the parent HZ sample, although the initial propylene selectivity of D-HZ was increased significantly from 15 to 23%, it dropped quickly to about 8% after 10 h, which is nearly equivalent to that of HZ. The trend of change of propylene selectivity with reaction time on the HZ-P catalyst is similar to that on HZ, i.e. increased firstly, reached a maximum and then decreased. Nevertheless, the maximum of the propylene selectivity on HZ-P (27%) is higher than that on HZ (24%); more importantly, the propylene selectivity decreased at a much slower rate and the reaction time lasted for propylene selectivity >10% was 100 h, about 8 times longer than that on HZ (12 h). For the D-HZ-P catalyst, the catalytic stability was further improved compared with HZ-P, although both catalysts exhibited the similar maximum of propylene selectivity (ca. 27%). The propylene selectivity on D-HZ-P catalyst at TOS = 100 h was 23%, which is significantly larger than that (10%) on the HZ-P catalyst. This result indicates that the combined modifications of HZSM-5 with alkali and P can greatly improve the catalytic stability.

The variation trend of butylene selectivity of each HZSM-5 sample is similar to propylene selectivity (Fig. 5b). It could be inferred that propylene and butylene might be produced through the parallel pathways and the common intermediate on the HZSM-

5 catalysts, in good agreement with the conclusion obtained by Aguayo et al. [35].

As presented in Fig. 5c and d, the ethylene selectivity of all the HZSM-5 catalysts increased with TOS, whereas, the selectivity for aromatics decreased with reaction time. As described by Song et al. [4] and Inoue et al. [18], lower surface acidity leads to the formation of more ethylene, while aromatics are promoted at higher acidity. During the ethanol conversion reaction, coke formed and preferentially covered the strong acidic sites of the catalyst. Thus, the selectivity variation trend of ethylene and aromatics can be explained by the deactivation of the strong acidic sites [31].

The reasons for the significantly improved stability of HZSM-5 zeolite catalyst co-modified with alkali and P for the selective conversion of bio-ethanol to propylene can be attributed to: (1) The new developed mesopores by alkali treatment. As well known, coke deposition is the main reason for the decreasing of propylene selectivity on HZSM-5 zeolite catalyst, and the coke formation mainly occurs in the secondary pores [36]. Therefore, the ability to tolerate the carbonaceous deposit is significantly improved due to the formation of new mesopores after modification with alkaline solutions (see Table 1). (2) The decreased amount of strong acid sites by modification with phosphorus. It was well documented that the strong acid sites are responsible for coke formation [37]. Thus, the formation of coke was efficiently prohibited due to the decreased amount of strong acid sites by modification with phosphorus (see Table 2), and consequently the stability of catalyst is improved significantly. The formation of coke prohibited by P modification was confirmed

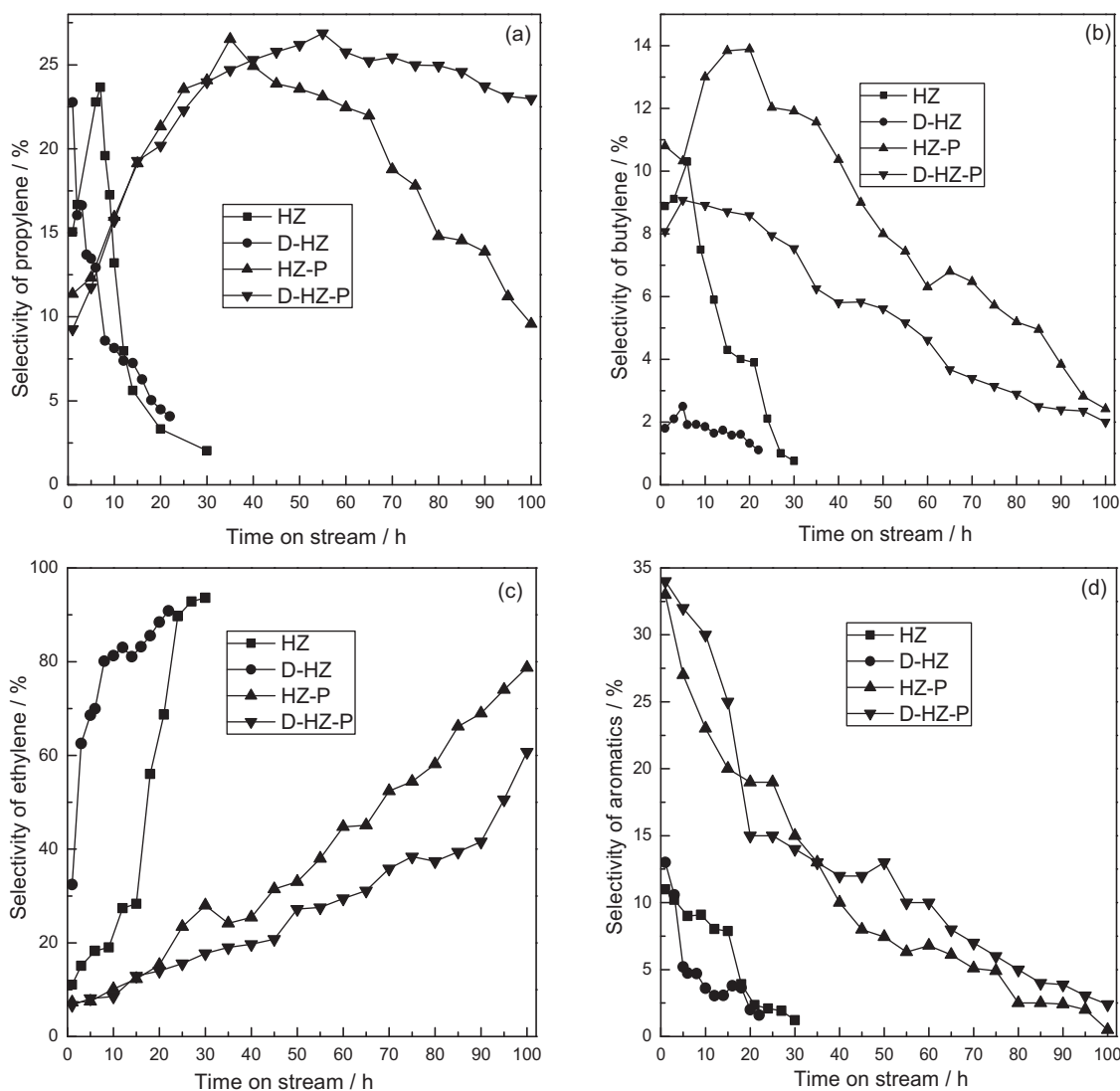


Fig. 5. Change of product selectivity vs. reaction time over the different HZSM-5 catalysts for bio-ethanol dehydration to propylene. (Reaction conditions: atmospheric pressure; $T = 500^\circ\text{C}$; ethanol concentration = 90 vol%; $\text{WHSV} = 3.3\text{ h}^{-1}$; ethanol conversion = 100%).

by the fact that the average carbon deposition rate on D-HZ-P catalyst is only half that on D-HZ as determined by TG technique, i.e. 1.2×10^{-3} and 2.5×10^{-3} g/g_{cat}h, respectively.

To investigate the reasons for deactivation of the HZSM-5 catalysts and the regeneration ability of the deactivated catalysts, the used catalysts were regenerated by calcining in air at 550°C for 2 h. The catalytic performance of the regenerated catalysts was evaluated under the same reaction conditions as the fresh catalysts. The results show that the propylene selectivity of the regenerated HZ and D-HZ catalysts was evidently lower than that of the corresponding fresh catalysts, indicating that dealumination of the ZSM-5 framework occurred on these two catalysts during the ethanol conversion process. On the contrary, the propylene selectivity of the regenerated HZ-P and D-HZ-P catalysts was completely recovered. This result indicates that the deactivation of the P modified HZSM-5 catalysts (HZ-P and D-HZ-P) was caused by carbon deposition but not by dealumination, which can be attributed to the enhanced hydrothermal stability of the framework aluminum by the modification of ZSM-5 zeolite with phosphorus [29,34]. Similar result was also reported by Takahashi et al. [11].

In order to compare our result with the literature data, the following available results of other authors were collected in Table 3.

Note that the experimental conditions used in various studies reported in literature may deviate from one to another, and especially mixture of ethanol and N_2 was used as feed in these studies while that of ethanol and water was used in the present study. Compared to these results, our catalyst seems to be promising, even if it still needs to be optimized.

4. Conclusions

The effect of modification by alkaline solution of NaOH, phosphoric acid and combined modification on the performance of HZSM-5 zeolite for the selective conversion of bio-ethanol to propylene was studied. The results indicate that the alkaline treatment with NaOH solution creates new mesopores, while phosphorous modification drastically decreases the amount of strong acid sites. The alkaline-phosphorous co-modified HZSM-5 catalyst exhibited significantly higher catalytic stability than the parent and singly modified ones, which could be attributed to the suitable acidity and pore structure.

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