

Para-selectivity of modified HZSM-5 zeolites by nitridation for ethylation of ethylbenzene with ethanol

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Abstract

The modification of HZSM-5 zeolite was carried out by nitridation of commercial HZSM-5 zeolites with flowing pure ammonia at high temperature. The modified HZSM-5 zeolites maintained high crystallinity and high specific surface areas of precursors testified by XRD, BET and SEM analysis. Compared with parent HZSM-5, the surface strong acid sites of modified HZSM-5 zeolites decreased severely as characterized by means of NH₃-TPD analysis and pyridine-IR spectroscopy shows that nitridation mainly occurred in Brønsted acid sites. The modified HZSM-5 zeolites exhibited much higher selectivity to *para*-diethylbenzene (DEB) and significantly enhanced stability than parent HZSM-5 when applied in the reaction of ethylbenzene ethylation with ethanol. The reduction of strong acid sites can suppress the isomerization of *para*-diethylbenzene and improve the *para*-selectivity. The effects of nitrogen contents in modified zeolites on the conversion and selectivity to *p*-DEB were also studied. © 2006 Elsevier B.V. All rights reserved.

Keywords: Nitridation; HZSM-5 zeolite; Modification; Para-selectivity; Ethylation of ethylbenzene with ethanol

1. Introduction

HZSM-5 zeolite could be the best catalyst for the reaction of ethylbenzene ethylation with ethanol to *para*-diethylbenzene because of its special shape selectivity and surface acidity. Many processes have been developed to modify its surface property in order to promote *para*-selectivity for alkylation and prevent coking deposition: for example, loading with oxide of P, Mg or B [1–6], coking with methanol [7], silylation with silicon alkoxide [8–11] using HZSM-5 zeolites of different crystal sizes [12], and use of metallosilicate zeolites with the MFI structure [13–15]. Modified HZSM-5 zeolites exhibit high *para*-selectivity than the parent zeolite.

The mechanism for the improvement of *para*-selectivity of the modified HZSM-5 zeolites has also been reported. Kaeding et al. proposed that the high *para*-selectivity of modified HZSM-5 zeolites for the alkylation or disproportionation was due to product shape selectivity; that is, the intracrystalline diffusivity of the *p*-isomer was much higher than that of the other two isomers [2,3,5]. Paparatto et al. reported that the *p*-isomer was

formed selectively inside the HZSM-5 channels in the ethylation of toluene while the isomerization of the *p*-isomer proceeded just on the external surfaces and that the improvement in *para*-selectivity by the modification was due to the inactivation of the acid sites on the external surfaces [12]. On the other hand, Yashima et al. proposed that the primary product in the alkylation was only the *p*-isomer due to restricted transition-state shape selectivity and that the improvement in *para*-selectivity by the modification of HZSM-5 was due to the suppression of the isomerization of primarily produced *p*-isomer [1,4,13]. However, most modified HZSM-5 zeolites give rise to control of the pore-opening size and simultaneously inactivation of acid sites on the external surface until now. Therefore, it is difficult to clarify the roles of both factors on improvement of *para*-selectivity.

Recently, nitridation was reported as a method for introducing basic sites into zeolites, and the nitridized zeolites can maintain the specific areas as well as good crystallinity of precursors [16–19]. However, the basicity of nitrogen-incorporated zeolites is less strong than that of nitridized amorphous phase because it is quite difficult for zeolites to react with ammonia due to their crystallinity and instability of framework [20]. Considering surface acid sites of zeolites can be changed by nitridation due to nitrogen atom incorporating into the framework of zeolites, we think that nitridation of zeolites could be a modification method

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for adjusting surface acidity of zeolites with keeping the porous property of parent zeolites at same time. Consequently, it is possible to investigate the influence of acid sites on the external surface of zeolite on para-selectivity alone with elimination of effects on pore-opening sizes.

In this paper, we will report para-selectivity of modified HZSM-5 zeolites, which were obtained by nitridation at high temperature, for the ethylbenzene ethylation with ethanol, and will discuss the effect of nitrogen incorporation into zeolites on their para-selectivity.

2. Experimental

2.1. Catalysts preparation

Modified HZSM-5 zeolites were obtained by nitridation of HZSM-5 zeolite (commercial HZSM-5 zeolite, Si/Al = 50) at 1073 K for 5 h, 10 h and 15 h, respectively. The zeolites were pre-treated at high temperature before being nitridized with ammonia. Typical nitridation process was carried out in a tubular quartz furnace in which zeolite was placed in a quartz boat and treated by flowing pure ammonia. The quartz tube with the sample was evacuated and flushed with N₂ several times before nitridation. At the end of the nitridation process, the sample was slowly cooled to room temperature under an N₂ flowing stream. The obtained samples were denoted by HZSM-5-5N, HZSM-5-10N and HZSM-5-15N, respectively.

2.2. Catalysts characterization

2.2.1. Nitrogen content measurement

The total nitrogen content of modified zeolites was detected by alkaline digestion with molten NaOH at 673 K, and the resulting NH₃ was absorbed with sulfuric acid solution which was then titrated by NaOH solution. The detailed procedure can be found in the literature [21].

2.2.2. XRD analysis

XRD analysis was carried out on a D/Max-2500 powder diffractometer (36 kV and 20 mA) using Cu K α ($\lambda = 1.54178 \text{ \AA}$) radiation from 5° to 40° with a scan speed of $2\theta = 4.0^\circ \text{ min}^{-1}$.

2.2.3. BET measurement

The surface areas of samples were obtained by nitrogen adsorption using a Micromeritics ASAP2010M instrument at 77 K (liquid nitrogen temperature) after outgassing the samples for 2 h under vacuum at 573 K.

2.2.4. SEM analysis

SEM images of the samples before and after nitridation were obtained for structural identification using a HITACHI S-3500N scanning electron microscope.

2.2.5. NH₃-TPD measurement

Acidity was measured by NH₃-TPD with a Micromeritics TPD/TPR 2900 equipment furnished with TCD. Typically, about 200 mg of the sample was pre-treated in helium at 973 K for 1 h

and then cooled to 373 K prior to the adsorption of NH₃ at this temperature. After saturated with NH₃, the catalyst was flushed with helium for 4 h to remove the physisorbed gas from the catalyst surface. Then the desorption pattern was recorded at a heating rate of 10 K/min from 373 K to 973 K.

2.2.6. Py-IR analysis

The surface acidity of samples was characterized by the IR spectrum of adsorbed pyridine on a Bruker VECTOR 22 FT-IR spectrophotometer. Samples were placed in the measurement cell and evacuated to remove the water located on the surface and in the pore of the zeolites. After the background spectrum of the samples was recorded, the valve of the pumping system was closed and the valve of the pyridine supply was opened for 15 min. The cell was subsequently evacuated again under 473 K for 15 min to remove physisorbed pyridine, and then the spectrum of adsorbed pyridine at room temperature was recorded.

2.2.7. TG analysis

TG analysis was conducted on a Setaram thermobalance TG-DTA 92 instrument using N₂ as the carrier gas at 30 ml/min about 20 mg of the sample. Temperature is raised at 5 K/min from room temperature to 973 K.

2.3. Catalytic activity evaluation

The evaluation of catalytic activity and selectivity was carried out on a fixed-bed microreactor at atmospheric pressure. About 0.6 g of the catalyst (mesh of 20–40) was placed in the isothermal region of the reactor. The reactants were fed into the reactor by a syringe infusion pump that could be operated at different flow rates. The reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller cum indicator. The products were passed through a water-cooled condenser and collected at a certain intervals and then analyzed in a SP-502 gas chromatograph equipped with a 0.25 mm \times 50 m OV101 capillary column.

3. Results and discussion

3.1. Physicochemical properties of samples

XRD patterns of HZSM-5 and nitrogen-incorporated HZSM-5 zeolite (0.96 wt% N) (Fig. 1) show changes in peak intensities after nitridation at high temperature. There is a slight decrease in peak intensities in the regions of 2θ (22–25°), whereas the increased peak intensities in the regions of 2θ (7–10°) were observed clearly. The relative crystallinity had no obvious variation for samples HZSM-5 and HZSM-5-10N, which indicated that nitridized zeolites still kept high crystallinity. Consequently, nitridation process does not result in the structural damage of HZSM-5 zeolites.

In addition, it was found that from the results of BET measurement shown in Table 1, the specific surface areas of modified HZSM-5 zeolites, nitridied at high temperature for different time, had no great change, which also confirmed that no obvious structural damages occurred during the high temperature

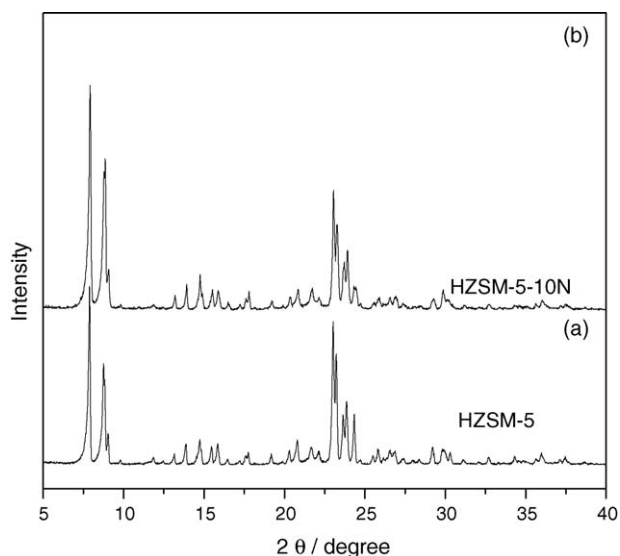


Fig. 1. XRD patterns of samples before and after nitridation: (a) HZSM-5 zeolite and (b) HZSM-5-10N zeolite.

treatment. Xiong et al. reported that the BET surface areas of nitrogen-incorporated SAPO-11 decreased deeply when nitridation was performed at 1073 K [22]. The reason could be that SAPO-11 molecular sieve has less thermal stability than HZSM-5 zeolite. However, the structure of modified HZSM-5 zeolite

Table 1
BET surface area and N content for the HZSM-5 and modified HZSM-5 zeolites

Catalysts	Nitridation time (h)	N (wt%)	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^a
HZSM-5	0	0	289
HZSM-5-5N	5	0.55	284
HZSM-5-10N	10	0.96	280
HZSM-5-15N	15	1.21	267

^a Nitridation condition: 800 °C; NH_3 flow rate 30 ml/min.

modified by nitridation could be damaged when nitridation temperature was above 1323 K [23].

Fig. 2 shows the SEM images of HZSM-5 zeolites before and after treated with ammonia. It can be seen that growth of crystal grains was induced by nitridation at 1073 K. The shape and dispersion of crystallites was almost maintained though a few smaller grains whose crystallinity was slightly low still existed.

Moreover, as displayed in Table 1, the nitrogen content in HZSM-5 zeolites modified by nitridation increased with nitridation time. The highest nitrogen content achieved up to 1.21% when zeolite was nitridized for 15 h; however, its surface area declined slightly. In conclusion, nitrogen-incorporated HZSM-5 zeolites still maintained the high crystallinity and high specific surface area of precursors after treating at elevated temperature.

NH_3 -TPD patterns of HZSM-5 and modified HZSM-5 zeolite (HZSM-5-10N) are shown in Fig. 3. The desorbed gas was only

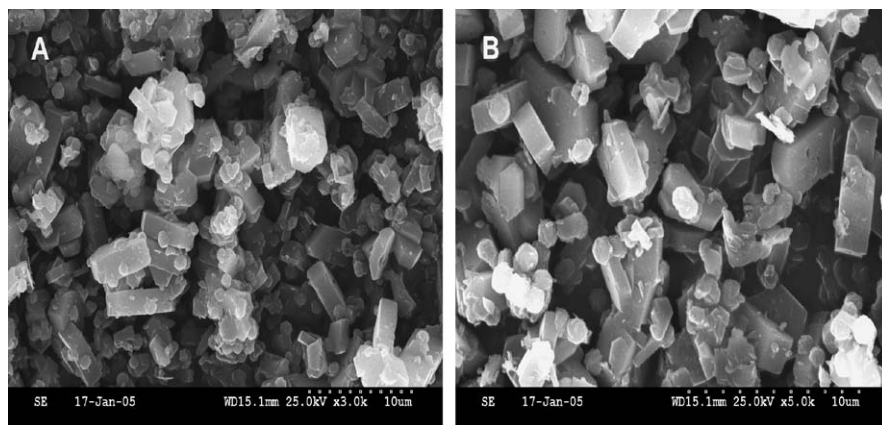


Fig. 2. SEM images of samples: (A) HZMS-5 and (B) HZSM-5-10N.

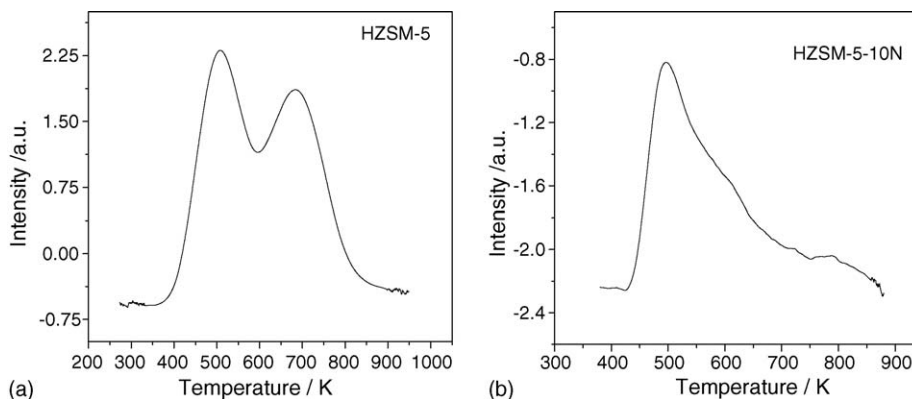


Fig. 3. The patterns of NH_3 -TPD of: (a) HZSM-5 and (b) HZSM-5-10N.

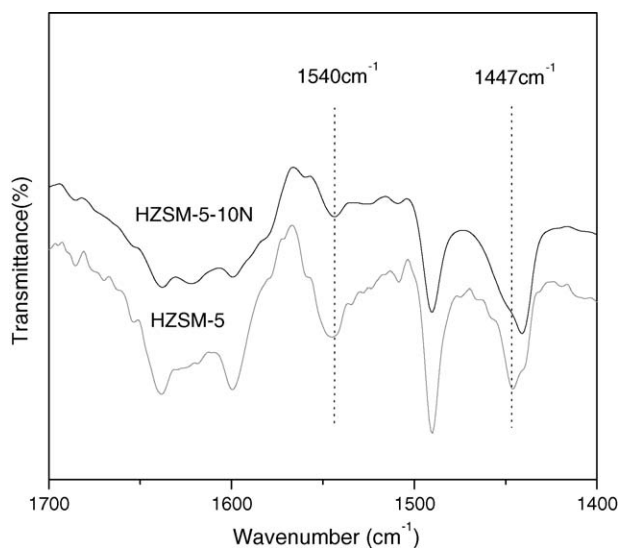


Fig. 4. IR spectra of pyridine adsorbed on HZSM-5 and HZSM-5-10N.

ammonia through the run. The HZSM-5 zeolite exhibited two peaks of NH_3 desorption. One at ca. 495 K corresponds to weak acid sites and the other at ca. 685 K corresponds to strong acid sites. The amount of strong acid sites was remarkably reduced for HZSM-5 zeolite modified by nitridation. The desorption peak at high temperature (ca. 685 K) disappeared while the lower temperature peak (ca. 495 K) was still maintained. It can be deduced that the strong acid sites were totally destroyed by nitridation and the weak acid sites were not affected. So the nitridation mainly occurred on strong acid sites. And the acid strength distribution of modified HZSM-5 zeolite was more homogeneous than parent materials.

As indicated by Py-IR spectra of HZSM-5 and modified HZSM-5 zeolite in Fig. 4, the peak at 1540 cm^{-1} representing Brønsted acid sites decreased sharply on HZSM-5 zeolite modified by nitridation, and Lewis acid sites (1447 cm^{-1}) also decreased slightly. From the results of Py-IR for samples before and after nitridation, it could be deduced that the changes of acidic sites of modified HZSM-5 zeolite were caused by substitution of nitrogen containing groups on Brønsted acidic sites during nitridation process. Zhang et al. [23] reported the evidence for N incorporation into the framework of ZSM-5 zeolite. The $\text{SiO}_3\text{-OH}$ phase, which belongs to Brønsted acid sites, in modified ZSM-5 zeolites disappeared while SiNO_3 phase formed as characterized by solid-state NMR. The result is consistent with acidity characterization by Py-IR shown in Fig. 4.

3.2. Catalytic activity evaluation

In the alkylation of ethylbenzene with ethanol on the HZSM-5 zeolites, the main aromatic products were *p*- and *m*-diethylbenzenes. The para-selectivity was defined as a fraction of the *p*-isomer in the diethylbenzene (DEB) produced. Ethylation of ethylbenzene with ethanol was carried on HZSM-5 and modified HZSM-5 zeolites (HZSM-5-10N) at 643 K. The feed ratio of ethylbenzene to ethanol was 2:1, and WHSV was 6 h^{-1} . The ethylbenzene conversion and *p*-DEB selectivity are plotted

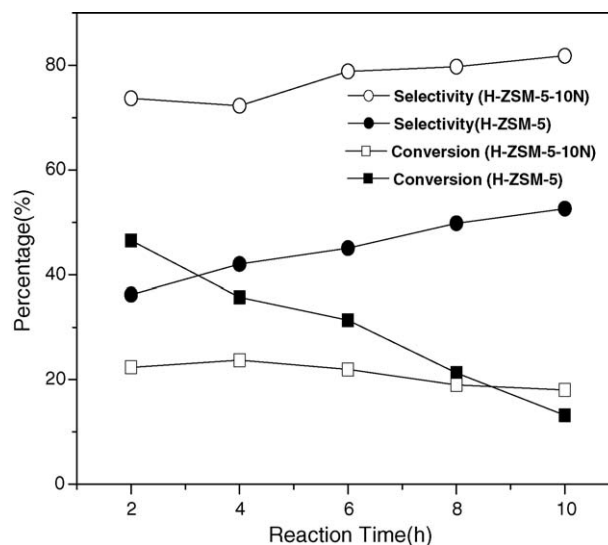


Fig. 5. Conversion of ethylbenzene and selectivity to *p*-DEB on various catalysts (temperature = 643 K; WHSV = 6 h^{-1} ; feed ratio (ethylbenzene:ethanol) = 2:1).

as a function of reaction time as shown in Fig. 5. A higher initial activity, decreasing rapidly with reaction time, was found over the parent HZSM-5, and the selectivity to *p*-DEB was typically low. In contrast, the selectivity to *para*-DEB over HZSM-5-10N was obviously enhanced from ca. 52% to ca. 84%, and its activity declined slightly with reaction time.

Ethylbenzene ethylation to diethylbenzene has been mostly concerned as a typical acid-catalyzed process. Strong surface acidity of HZSM-5 is in favor of ethylbenzene conversion but not favorable for selectivity to *p*-DEB. Many researchers suggest that the high para-selectivity for the alkylations of monoalkylbenzenes is caused by the shape selectivity of the modified ZSM-5 zeolite [2,3,5]. According to Paparatto et al. [12], the *p*-isomer was formed selectively inside the HZSM-5 channels in the reaction at first, while the isomerization of the *p*-isomer proceeded just on the external surfaces and that the improvement in the para-selectivity by the modification was due to the inactivation of the acid sites on the external surfaces. On the other hand, Yashima et al. proposed that high para-selectivity is due to the reduction of strong acid on surface suppressing the isomerization of *p*-isomer that was the only primary product [1]. In the present study, the surface strong acid sites in modified HZSM-5 zeolites lost obviously as characterized by NH_3 -TPD (see in Fig. 3), and the specific surface area and structure of modified HZSM-5 zeolites had no changes after nitridation tested by BET and XRD analysis (see in Table 1 and Fig. 1). Therefore, the reduction of acidity could be responsible for the improvement of the para-selectivity because the isomerization of *para*-DEB was suppressed due to the absence of strong acid sites. From the results described above, we conclude that the weaker acid strength of catalysts provides the higher para-selectivity and that the acid strength is closely related to the para-selectivity other than the pore-opening size as suggested by Kim et al. [13].

Ethylbenzene conversion and selectivity to *p*-DEB on modified HZSM-5 zeolites with different nitrogen contents are shown in Figs. 6 and 7. Compared to the parent HZSM-5, modi-

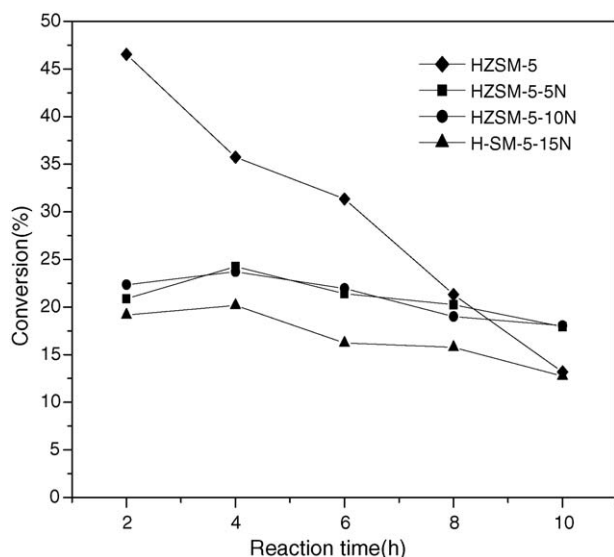


Fig. 6. Conversion of ethylbenzene over HZSM-5 and nitrogen-incorporated HZSM-5 zeolites (temperature = 643 K; WHSV = 6 h⁻¹; feed ratio (ethylbenzene:ethanol) = 2:1).

modified HZSM-5 zeolites exhibited much more stable activity and improved para-selectivity in spite of lower initial conversion. The selectivity to *p*-DEB improved with the increase in the nitrogen content and the ethylbenzene conversion decreased at the same time. A relationship between the nitrogen content of samples and ethylbenzene conversion is shown in Fig. 6, which suggested that the acidity of modified HZSM-5 zeolites is related to the nitrogen content because the acidity of catalysts is favorable for the conversion of ethylbenzene. The higher nitrogen content corresponds to the less acidic sites probably due to more Brønsted acid sites reduced by nitrogen substituting silanol groups for the high nitrogen content samples [23]. Fig. 7 shows that the sample containing the highest nitrogen content (1.21%) presented very high selectivity to *p*-DEB (>90%) since the iso-

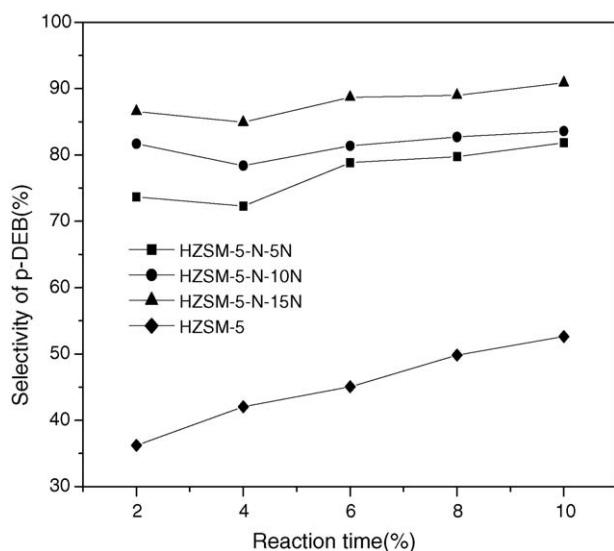


Fig. 7. Selectivity to *p*-DEB over HZSM-5 and modified HZSM-5 zeolites (temperature = 643 K; WHSV = 6 h⁻¹; feed ratio (ethylbenzene:ethanol) = 2:1).

Table 2

The TG analysis for HZSM-5 and modified HZSM-5 zeolites after reaction

	Samples			
	HZSM-5	HZSM-5-5N	HZSM-5-10N	HZSM-5-15N
Weight loss (wt%)	7.2	5.8	3.6	2.5

merization of *p*-isomer on the surface of catalysts was restricted which requires very strong acid sites [13]. Therefore, nitridation can be considered as an effective modification method for improving para-selectivity of HZSM-5 zeolites for ethylbenzene ethylation with ethanol.

The TG analysis of modified HZSM-5 zeolites shows that less coke deposited on the modified HZSM-5 zeolites than on the parent HZSM-5 (see in Table 2). It is well known that strong acidity leads to more extensive coking, causing the rapid inactivation of catalysts. From Table 2, it can be seen that coke deposition decreased with increasing nitrogen content of samples, indicating that the acidity of the modified HZSM-5 zeolites was weaker than that of the parent zeolite. This is consistent with the results that the conversion was more stable over the modified zeolites as illustrated in Fig. 6. The changes on surface acidity of modified HZSM-5 zeolite before and after reaction were also investigated by Py-IR (shown in Fig. 8). Fig. 8 shows that Lewis acidic sites decreased clearly after reaction while no changes of Brønsted acidic sites were observed. Based on these results, we propose that the ethylbenzene conversion occurred on both Brønsted acid sites and Lewis acid sites. When HZSM-5 zeolites were modified by nitridation, most of Brønsted acid sites were covered due to nitrogen incorporation. Then the ethylbenzene conversion was low compared with the unmodified zeolite and Lewis acid sites make more contribution to conversion. The ethylbenzene conversion decreased slightly with the reaction time due to coke deposition on Lewis acidic sites during reaction process.

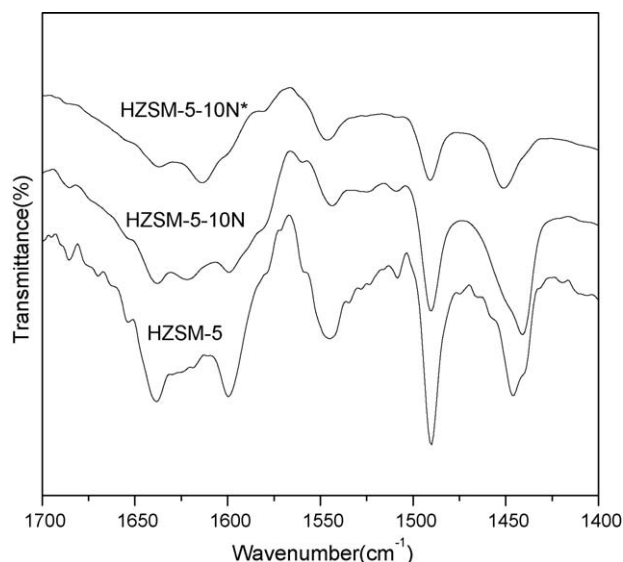


Fig. 8. IR spectra of pyridine adsorbed on HZSM-5, HZSM-5-10N (before reaction) and HZSM-5-10N* (after reaction).

4. Conclusion

HZSM-5 zeolites modified by nitridation were obtained by treating HZSM-5 with ammonia at elevated temperature. After nitridation, the acid sites of zeolites changed dramatically while high crystallinity and high specific surface areas were maintained. Modified HZSM-5 zeolites exhibit higher selectivity to *p*-DEB and more stable ethylbenzene conversion than the unmodified zeolite. The improvement of para-selectivity by nitridation of HZSM-5 is due to the decrease in strong acid sites which cause isomerization of *para*-diethylbenzene, not due to changes of the size of zeolite channel openings. Both Brønsted acid sites and Lewis acid sites provide active sites for ethylbenzene conversion, and since Brønsted acid sites decreased greatly after nitridation, Lewis acid sites make more contribution to ethylbenzene conversion after HZSM-5 zeolites were nitridized. A close relationship between the nitrogen content and para-selectivity of samples was observed. The modified HZSM-5 zeolite with 1.21 wt% N exhibits a para-selectivity higher than 90%.

Acknowledgements

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