Surface acidity of H-beta and its catalytic activity for alkylation of benzene with propylene

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The acidity of H-beta zeolites with SiO_2/Al_2O_3 ratios ranging from 20 to 350 was characterized by NH_3-TPD profiles and FTIR spectra of adsorbed pyridine. As SiO_2/Al_2O_3 ratios of the H-beta zeolites increased, NH_3-TPD acidic amount of the samples is decreased. The IR bands of the adsorbed pyridine on the zeolites are also decreased with the increased SiO_2/Al_2O_3 ratios. The batch reaction of propylene and benzene was carried out in liquid phase at 423 K over H-beta zeolites. The selectivity to isopropylbenzene was high. The catalytic activity of H-beta zeolites is in direct proportion to the acidic amount of the zeolites in general. H-beta zeolite of $SiO_2/Al_2O_3 = 27$, which contains the highest amount of Brønsted acid sites as indicated by FTIR spectra of adsorbed pyridine, is the most reactive catalyst in the alkylation reaction. In continuous liquid-phase reactions, high propylene conversion and isopropylbenzene selectivity can be achieved at 413–453 K with benzene to propylene mole ratio from 4 to 8. The catalytic activity and selectivity of the H-beta zeolite do not change after 1100 h of reaction.

KEY WORDS: H-beta zeolites; NH_3-TPD; IR spectra of adsorbed pyridine; alkylation of benzene; isopropylbenzene

1. Introduction

Zeolite beta was applied as solid acid catalyst for aromatic alkylation and disproportionation [1–6], aromatic acylation and Fries rearrangement [7–10], indole synthesis [11], aromatic nitrition [12], aliphatic alkylation [13]. H-beta as a catalyst for alkylation of benzene with propylene was developed recently. In comparison with the traditional process using diatomite supported phosphoric acid catalyst, the catalytic activity (also productivity) of H-beta is six times higher as the diatomite supported phosphoric acid catalyst.

In this paper, surface acidity of zeolite beta samples of different Si/Al ratios was characterized with NH_3-TPD profiles and IR spectra of pyridine adsorbed on the surface. These beta zeolites were applied as catalysts for the alkylation of benzene with propylene in liquid phase. The catalytic activity is related to the surface acidity of these zeolites.

2. Experimental

Zeolite beta samples were provided by Changling company which were synthesized using TEAOH as template agent. The SiO_2/Al_2O_3 ratios of these samples are 20, 27, 80, 100 and 350.

The H-form of zeolite beta was prepared through the following process: 2 g of as-synthesized beta zeolite was first calcined at 913 K for 8 h. The calcined sample was then ion-exchanged with 20 ml of 0.6 M NH_4NO_3 solution at 373 K for 1 h. The ion-exchange process was repeated three times. Then the sample was dried at 383 K and calcined at 913 K for 4 h.

NH_3-TPD experiment was carried out through the following process: 0.2000 g of sample was heated at 500 °C for 2 h. The temperature was reduced to 120 °C, the sample was contacted with NH_3, vacuumized for 30 min, and then the temperature was raised at a rate of 25 °C/min to 600 °C in 40 ml/min of helium flow. The desorbed NH_3 was analyzed by GC using the external standard method to calculate the amount of acid sites on the samples.

IR spectra were collected on a NICOLET IMPACT 410 spectrometer. A pure zeolite disk was treated at 500 °C under 1.33×10^{-3} Pa for 5 h. After cooling to room temperature the sample was contacted with pyridine vapor and then treated at 150 °C under high vacuum for 30 min. IR spectra were collected at 273, 298, 423, 573, 673 and 773 K.

Batch reactions of benzene and propylene were performed in an autoclave. 78 g of benzene and 6.3 g of liquidized propylene were charged into the reactor. 0.4 g of freshly calcined (4 h, 773 K) catalyst was added. The reactor was pressurized with nitrogen. The temperature was raised to 423 K and the reaction took place under stirring. The pressure was maintained at 2.7–3 MPa. Continuous liquid-phase experiments were carried out in a fixed-bed, up-flow reactor at 2.7–3 MPa. The binder-free catalysts were granulated by compression followed by grinding, the 0.2–0.6 mm fraction was packed into the 8 mm stainless-steel reactor and *in situ* activated in dry nitrogen flow (10 ml/min) at 573 K for 5 h. In all experiments samples were periodically collected and off-line analyzed by GC (SQ 206) using a 2 mm × 2 m column.

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3. Results and discussion

3.1. Characterization of acidity with NH_3-TPD analysis and IR spectra of adsorbed pyridine

Temperature-programmed desorption of ammonia is a useful method to determine the surface acid sites of solid acids. The amount of desorbed ammonia can be considered as the amount of the acid sites on the sample. The strength of the acid sites also can be determined by desorption temperature. The higher the ammonia desorption temperature is, the stronger the acid sites are.

NH_3-TPD profiles of H-beta of different SiO_2/Al_2O_3 ratios are illustrated in figure 1. Acidic amount determined by the amount of desorbed ammonia (peak area) and acidic strength determined by desorption peak position (temperature) are summarized in table 1.

In general, as the SiO_2/Al_2O_3 ratio of the H-beta zeolites is increased, the total acid sites amount is decreased. There are two ammonia TPD peaks in the profiles, which means there are weak acid sites and strong acid sites on the zeolites. On H-beta of SiO_2/Al_2O_3 ratio 10, weak acid sites are dominant and strong acid sites just form a little shoulder peak. As the SiO_2/Al_2O_3 ratio is increased, the amount of weak acid sites decreases more quickly than the amount of strong acid sites. For the H-beta of SiO_2/Al_2O_3 ratios 100 and 350, strong acid sites form the main peak on the NH_3-TPD profiles. As the SiO_2/Al_2O_3 ratio is increased, the tops of the two ammonia TPD peaks also shift to lower temperatures.

In the high temperature part of some NH_3-TPD profiles, there are desorption peaks that are due to dehydroxylation of the zeolites, as reported by Camiloti *et al.* [14]. This part of desorption peaks are not calculated into the total acidic amount.

FTIR spectra of pyridine adsorbed on H-beta were collected at different temperature. FTIR spectra of pyridine adsorbed on H-beta-1 ($SiO_2/Al_2O_3 = 20$) are illustrated in figure 2. As the temperature rose, IR adsorption bands of pyridine became weaker, which means part of the pyridine molecules adsorbed on weak acid sites desorbed as the temperature rose. FTIR spectra of pyridine adsorbed on different H-beta zeolites are compared at 423 and 773 K in figures 3 and 4.

As shown in figures 3 and 4, the area of the FTIR signals of pyridine decreases as the SiO_2/Al_2O_3 ratio is increased, which indicates the amount of acid sites in the H-beta zeolites decreases as the alumina content in zeolites decreases. IR signals of pyridinium ions (1546 and 1636 cm^{-1}), which are formed by interaction of pyridine and Brønsted acid sites, exist in all IR spectra even at high temperature, which means Brønsted acid sites exist in all the H-beta samples of various SiO_2/Al_2O_3 ratios at different temperatures. IR signals of pyridine adsorbed on Lewis acid sites (1455 and 1621 cm^{-1}) also exist in all IR spectra at different temperatures.

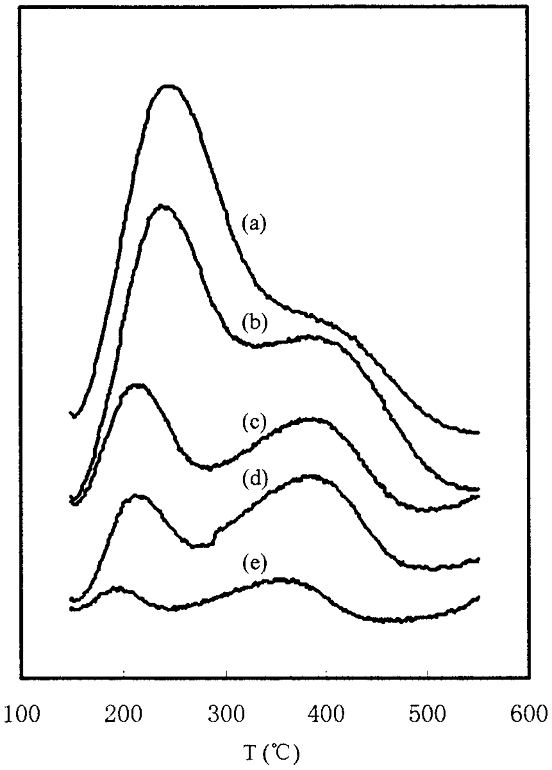


Figure 1. NH_3-TPD profiles of (a) H-beta-1 ($SiO_2/Al_2O_3 = 20$), (b) H-beta-2 ($SiO_2/Al_2O_3 = 27$), (c) H-beta-3 ($SiO_2/Al_2O_3 = 80$), (d) H-beta-4 ($SiO_2/Al_2O_3 = 100$) and (e) H-beta-5 ($SiO_2/Al_2O_3 = 350$).

Table 1
NH_3-TPD data of H-beta of different SiO_2/Al_2O_3 ratios.

Sample	SiO_2/Al_2O_3 (mol)	TPD acidic amount (mmol/g)	TPD acidic strength (°C) Weak	Strong
H-beta-1	20	0.808	252	418
H-beta-2	27	0.801	247	402
H-beta-3	80	0.337	222	396
H-beta-4	100	0.405	220	388
H-beta-5	350	0.118	198	363

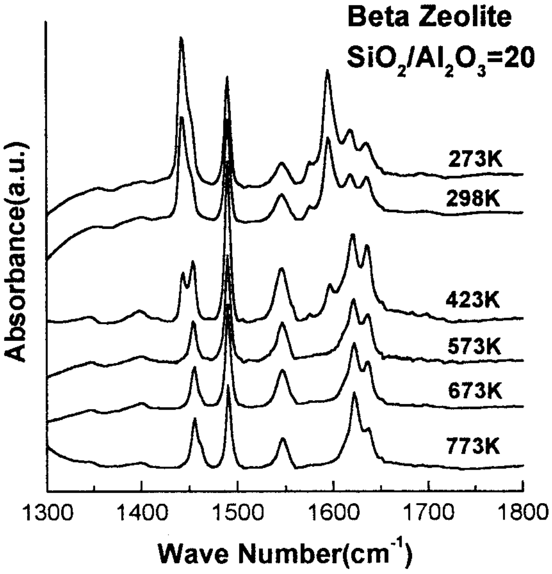


Figure 2. FTIR spectra of pyridine adsorbed on H-beta-1 ($SiO_2/Al_2O_3 = 20$) at different temperatures.

3.2. Liquid-phase batch reactions

Isopropylbenzene is an important intermediate for production of phenol and other chemicals. Traditionally it is produced by two methods [15]: (1) Gas-phase reaction of benzene and propylene at 250 °C at 2–2.5 MPa catalyzed by the diatomite supported phosphoric acid catalyst. This method is non-corrosive, but the productivity of the catalyst is low. Supported phosphoric acid catalyst cannot catalyze the trans-alkylation of di- or triisopropylbenzenes, so multi-isopropylbenzenes cannot be fed back to convert to mono-isopropylbenzene. The overall yield is relatively low. (2) Liquid-phase alkylation of benzene at 90–95 °C with propylene at 90–95 °C catalyzed by $AlCl_3$. This method has high yield and productivity, but the catalyst is corrosive and easy to lose.

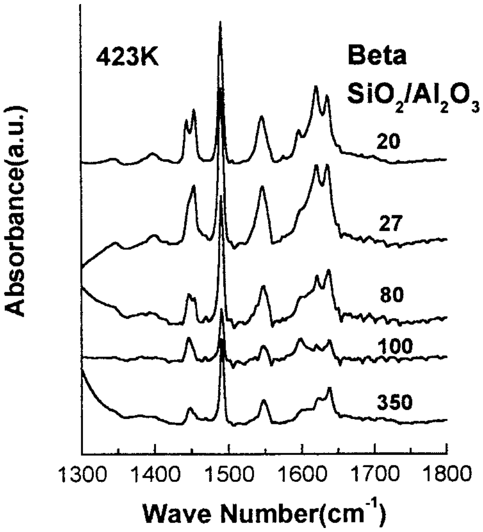


Figure 3. FTIR spectra of pyridine adsorbed on H-beta zeolites of different SiO_2/Al_2O_3 ratios at 423 K.

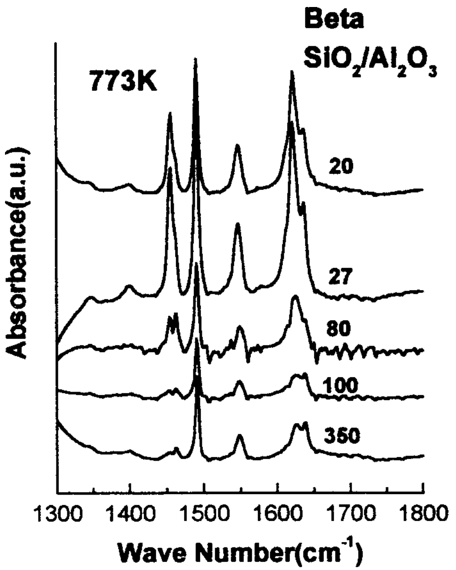


Figure 4. FTIR spectra of pyridine adsorbed on H-beta zeolites of different SiO_2/Al_2O_3 ratios at 773 K.

In recent years liquid-phase reaction of benzene and propylene catalyzed by H-beta has been developed as a new process to produce isopropylbenzene. H-beta as a solid acid is non-corrosive and it can catalyze the trans-alkylation of multi-isopropylbenzenes with benzene. The new process has many advantages when compared with the traditional processes.

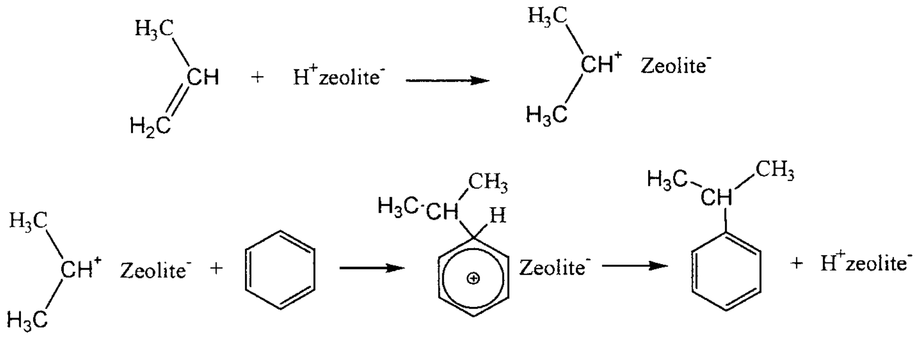
Batch reactions of benzene and propylene over different H-beta zeolites are studied and the reaction results are collected in table 2. The alkylation reactions are highly selective to isopropylbenzene over these zeolite catalysts. In general, H-beta zeolite with higher Al_2O_3 content is more reactive in this reaction.

This catalytic alkylation reaction is supposed to be catalyzed by Brønsted acid sites on the H-beta zeolites (scheme 1). The catalytic activity of H-beta zeolites for the alkylation reaction is related to the amount of acid sites on the zeolites. The reaction rate of benzene with propy-

Table 2
Batch reaction of benzene with propylene over H-beta zeolites of different SiO_2/Al_2O_3.[a]

Catalyst	SiO_2/Al_2O_3 (mol)	Conversion of benzene (%)	Product selectivity (%)		
			Isopropylbenzene	Diisopropylbenzenes	Other
H-beta-1	20	12.1	91.8	7.8	0.4
H-beta-2	27	12.9	92.4	7.3	0.3
H-beta-3	80	6.6	91.9	7.9	0.2
H-beta-4	100	5.2	92.7	7.1	0.2
H-beta-5	350	2.6	93.1	6.9	–

[a] Reaction conditions: 78 g (1 mol) of benzene, 6.3 g (0.15 mol) of propylene, 0.4 g of catalyst, 423 K, 2.7–3 MPa, 1 h.



Scheme 1.

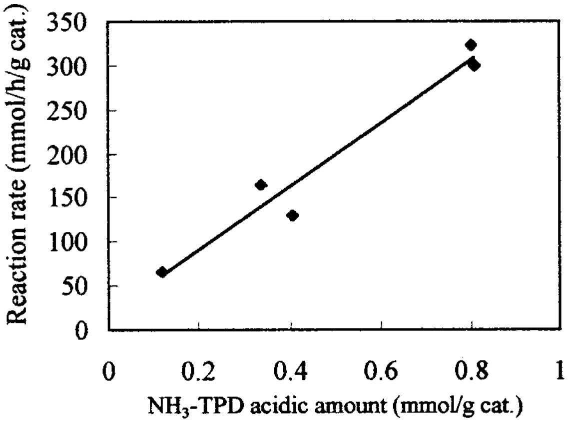


Figure 5. Relationship between reaction rate of benzene propylation over H-beta zeolites and the NH_3-TPD acidic amount of the zeolites.

Table 3
Continuous liquid-phase reactions of benzene with propylene under different conditions.[a]

Reaction temperature (K)	B/P[b]	Conversion of benzene (%)	Conversion of propylene (%)	Selectivity of IPB[c] (%)
403	6	15.7	98.4	95.3
413	4	23.1	98.4	93.6
418	6	15.6	100	94.8
423	6	15.8	100	94.6
433	4	23.0	100	91.3
433	8	11.9	100	94.5
443	4	23.0	100	91.3
443	6	15.4	100	91.7
453	8	12.5	100	92.6

[a] The reaction is carried out over H-beta-2 ($SiO_2/Al_2O_3 = 27$) catalyst. Pressure 2.7–3 MPa, WHSV 2 h^{-1}, time 20 h.
[b] B/P is the benzene to propylene mole ratio.
[c] IBP is isopropylbenzene.

lene over H-beta catalyst is plotted with the NH_3-TPD acidic amount of the zeolite in figure 5.

In general, the reaction rate is in direct proportion to the amount of the acid sites in the catalysts. But there are two exceptions. TPD acidic amount of H-beta-1 ($SiO_2/Al_2O_3 = 20$) is larger than that of H-beta-2 ($SiO_2/Al_2O_3 = 27$), but the catalytic activity of H-beta-1 is lower than that of H-beta-2. However, from the IR spectra of pyridine adsorbed on the H-beta zeolites, H-beta-2 contains more Brønsted acid sites than H-beta-1. This must be the reason why H-beta-2 is more reactive than H-beta-1 in the alkylation reactions. For the same reason, TPD acidic amount of H-beta-3 ($SiO_2/Al_2O_3 = 80$) is smaller than that of H-beta-4 ($SiO_2/Al_2O_3 = 100$), but there are more Brønsted acid sites in the H-beta-3 than in the H-beta-4 indicated by IR spectra of adsorbed pyridine, and the catalytic activity of H-beta-3 is higher than that of H-beta-4.

3.3. Continuous liquid-phase reactions

Continuous liquid-phase reactions were carried out to determine the best reaction conditions and the rate of the catalysts deactivation. H-beta-2 was applied as catalyst. Results obtained in continuous liquid-phase reactions of benzene with propylene under different conditions are collected in table 3. As the temperature varies from 413 to 453 K and the mol ratio of benzene to propylene varies from 4 to 8, good reaction results can still be achieved. The alkylation reaction over H-beta is not affected by reaction conditions too much if the reaction conditions are kept within a range.

To determine the rate of catalyst deactivation, continuous liquid-phase reaction was carried out at 453 K for 1100 h. The results are collected in table 4. The conversion of propylene and the selectivity to isopropylbenzene was still high after 1100 h. The catalyst is very stable in this reaction. We compare the IR spectra of pyridine adsorbed on H-beta-2 catalyst before and after the 1100 h of reaction (vacuumized at 673 K). The peak area of the IR band at 1546 cm^{-1} (Brønsted acid) is 3.11 for the fresh catalyst and 2.79 for the used catalyst; the peak area of the IR band at 1455 cm^{-1} (Lewis acid) is 2.53 for the fresh catalyst and 2.41 for the used catalyst. After the reaction the change of acid sites in the catalyst is small.

Table 4
Catalytic properties of H-beta-2 for long-time continuous liquid-phase reactions.[a]

Reaction time (h)	Conversion of propylene (%)	Selectivity of IPB[b] (%)
20	100	92.6
92	100	92.4
164	99.3	91.9
236	96.8	91.5
308	96.0	93.2
380	99.1	91.9
452	96.6	92.3
524	99.8	91.9
596	97.6	92.0
668	97.5	91.5
740	98.0	92.5
812	95.6	92.4
884	95.3	92.4
956	98.3	91.2
1028	98.5	91.7
1100	97.0	91.8

[a] Reaction conditions: temperature 453 K, pressure 2.7–3 MPa, WHSV 2 h^{-1}, benzene : propylene = 6 : 1.

4. Conclusion

NH_3-TPD profiles of H-beta zeolites show there are strong acid sites (high TPD temperature) and weak acid sites (low TPD temperature) in the zeolites. When SiO_2/Al_2O_3 ratio of the zeolites is increased, the total TPD acidic amount (peak area of NH_3-TPD profile) decreases in general. The amount of weak acid sites decreases more quickly when the SiO_2/Al_2O_3 ratio of the zeolites is increased. FTIR spectra of pyridine adsorbed on the H-beta zeolites show there are Brønsted acid sites and Lewis acid sites in all the H-beta samples at temperature varied from 273 to 773 K. The liquid-phase reactions of benzene and propylene over

H-beta zeolites are highly selective to isopropylbenzene. In general, the catalytic activity of H-beta zeolites is in proportion to NH_3-TPD acidic amount in the zeolites. H-beta-2 ($SiO_2/Al_2O_3 = 27$), which has the highest Brønsted acid sites content as shown by FTIR spectra of adsorbed pyridine, is the most reactive catalyst for the propylation of benzene. H-beta-2 catalyst is also very stable in the liquid-phase alkylation reaction and its catalytic activity and selectivity are almost unchanged after it has catalyzed the reaction at 453 K for 1100 h.

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