Selective synthesis of ethylamine over β zeolite

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Received 24 September 1993; accepted 17 March 1994

Ethylamine is selectively produced in the amination of ethanol with ammonia over Hβ zeolite.

Keywords: β zeolite; ethanol amination; selectivity

Beta zeolite was first synthesized by Mobil in 1967 [1]. Owing to the eluded determination of its structure and the discovery of ZSM-5, the application of this zeolite was almost in a state of silence during nearly twenty years. The structure of beta was not known clearly until modern techniques such as high-resolution electron microscopy, electron diffraction and computer-assisted modelling [2,3] were used. The special properties of this zeolite (such as large pores without cages, rich silica and high thermostability) enhance people's interest. The conversions of aromatics [4–8] and hydrocarbons [9,10] have been extensively investigated. The studies of this zeolite in other aspects, however, have received little attention.

It is well-known that ethylamine is a very important intermediate for medicaments, dyes and surface active agents. It is difficult to obtain selectively the amination of ethanol with ammonia over conventional catalysts such as some zeolites and γ-Al_2O_3 [11,12], the industrial catalyst. In this paper, we first report the amination of ethanol with ammonia over β zeolites and compare the results with those over HY, HM, HZSM-5 and γ-Al_2O_3 catalysts.

The parent sample, TEA-β, was calcined in air at 550°C for 5 h in order to remove the TEA cation from the zeolite, then the sample was exchanged three times with 2 M NH_4Cl solution at 75°C to obtain Hβ(E1). Hβ(E1) was washed with

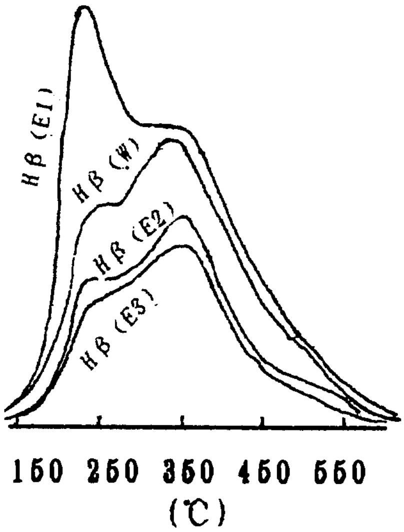

Fig. 1. NH_3-TPD spectra of the samples.

0.1 M HCl solution at room temperature until it was free of aluminium ions in the filtered solution; the washed sample was denoted as Hβ(W). Hβ(E2) and Hβ(E3) were obtained from the calcined samples by exchanging twice and five times with 0.3 M HCl solution for 4 and 10 h, respectively. The samples modified with H_3PO_4, $Mg(NO_3)_2$ and $La(NO_3)_3$ were obtained using the common impregnation method, the amount of impregnation is 2 wt%. All the samples containing chloride were washed until they were free of chloride ions, dried and calcined at 550°C in

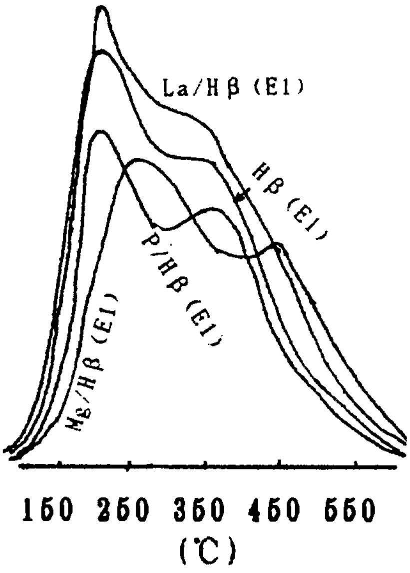

Fig. 2. NH_3-TPD spectra of the samples.

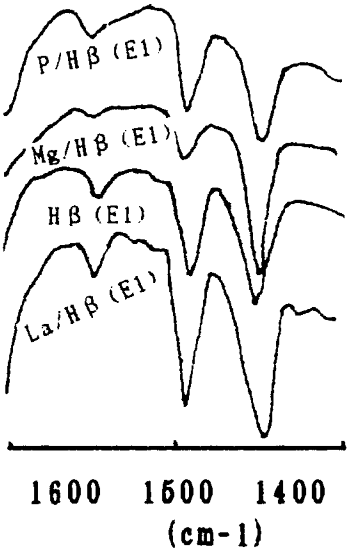

Fig. 3. Pyridine adsorption IR spectra of the samples.

air for 5 h before use. The NH_3-TPD spectra and pyridine adsorption IR spectra of the samples are shown in figs. 1–3. Some properties of these samples are listed in table 1. The reaction was conducted in a continuous flow reactor packed with 0.50 g catalyst, the sample was pretreated for 1 h with ammonia at reaction temperature before admitting ethanol. Analysis of the products was carried out by means of gas chromatography using a packed column [13].

The effects of the catalysts on the amination of ethanol with ammonia were carried out under the conditions of 410°C, $NH_3/C_2H_5OH = 3:1$ and WHSV = 8 h^{-1}. The conversion of ethanol and the selectivity to ethylamine

Table 1
Some acid properties of the samples

Sample	Acid amount [a] (mmol/g-cat)	T_{max} (°C)	T_{min} (°C)	B [b]	L [b]	L/(L + B) [c]	Percent of strong acid amount (>300°C)
Hβ(E1)	0.818	349	241	0.797	3.690	0.837	53.63
Hβ(W)	0.460	362	263	0.136	3.655	0.960	63.00
Hβ(E2)	0.300	361	250	0.063	2.552	0.991	64.07
Hβ(E3)	0.280	361	255	0.058	2.107	0.990	63.53
P/Hβ(E1)	0.600	346	241	0.173	1.988	0.649	52.37
Mg/Hβ(E1)	0.660	450	300	0.136	3.706	0.982	70.56
La/Hβ(E1)	0.850	360	241	0.277	3.439	0.762	54.94

[a] The results of NH_3-TPD.

[b] Integrated absorbance/g s.

[c] Determined as in ref. [14].

(ethene) over the tested catalyst do not change with time on stream. The results are given in table 2. From the activities and selectivities over the washed and exchanged samples it can be seen that the order of the conversion of ethanol and the selectivity to ethene is as follows: Hβ(E1) > Hβ(W) > Hβ(E2) ≈ Hβ(E3); to the contrary, the selectivity to ethylamine increases and is more than 80% over the samples exchanged with 0.3 M HCl solution, Hβ(E2) and Hβ(E3). The differences between the activities and the selectivities over the modified samples were also investigated; the Hβ(E1) zeolite modified with P favors ethanol dehydration to produce ethene. However, the increasing conversion of ethanol and selectivity to ethylamine were found after the Hβ(E1) zeolites were modified with La and Mg, respectively. Especially for the Hβ(E1) zeolite modified with Mg, the formation of ethene is hindered and the sample shows good catalytic property in the amination of ethanol with ammonia. Correlating the results of amination and the acid properties of the tested samples (figs. 1–3 and table 1), we suggest that the activity and the ethylamine (ethene) selectivity of the sample are related to the acid amount (especially L (Lewis) acid amount) and the relative strength of L acid sites, respectively. Namely, the more the acid amount (especially L acid amount), the higher the conversion of ethanol, while the concentration of ethylamine increases with increasing value of L/(L + B) (B, Brønsted acid amount) and percentage of strong acid sites on the sample. Compared with the other samples, the sample modified with Mg shows high activity and excellent selectivity for ethylamine, which is due to its more and relatively stronger L acid sites on the sample. From the results of ethanol amination over HY, HZSM-5, HM and γ-Al_2O_3 samples it can be found that the ethylamine selectivities over these catalysts are much lower than those over β zeolites. Thus, β zeolite is an excellent potential catalyst for the amination of ethanol with ammonia to produce selectively ethylamine because of its special acid properties.

Table 2
The effects of the catalysts on the amination of ethanol

Sample	Si/Al	Conversion of ethanol (%)	Selectivity (%)	
			ethylamine	ethene
Hβ(E1)	17.23	70.72	68.52	31.28
Hβ(W)	29.31	53.52	74.45	25.55
Hβ(E2)	34.20	36.43	80.70	19.30
Hβ(E3)	52.20	30.00	80.34	19.64
P/Hβ(E1)	17.23	42.33	59.80	40.20
Mg/Hβ(E1)	17.23	72.36	78.80	21.20
La/Hβ(E1)	17.23	75.00	70.90	29.10
HY	3.25	96.12	34.00	67.00
HZSM-5	18.03	57.50	42.80	57.20
HM	5.59	51.50	53.33	46.67
γ-Al_2O_3	–	98.00	28.72	71.28

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