

Selective Synthesis of Dibutylamine over Na β Zeolite Catalyst

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Abstract : The present investigation describes the study of catalytic activity of different forms of β zeolite catalysts for the synthesis of butylamines by the reaction of n-butyl alcohol and ammonia. It is observed that Na β zeolite showed the highest catalytic activity from among the catalysts investigated and showed very high selectivity towards dibutylamine.

Introduction

Amines are industrially made by the reaction between alcohol and ammonia [1]. Aliphatic amines are of considerable importance and find application in almost every field of modern technology, agriculture and medicine. Methanol and ethanol are probably the most commonly studied alcohols [2-6] for the ammonolysis reaction. The ammonolysis of butyl alcohols has also been investigated over various catalysts such as Pt on silica gel and active carbon [7], Al₂O₃ [8], and metal oxide mixtures [9,10]. Zeolites are being used as catalysts in various reactions because of their acidic as well as basic properties and microporous structures [11,12]. Zeolites have been investigated for the amination of butyl alcohols [13-15]. Ammonolysis of n-butyl alcohol on ZSM-5 has showed the formation of butylamines [14]. The activity of NaY zeolite for the ammonolysis of n-butyl alcohol is attributed to the presence of Na⁺ ions in the zeolite lattice [15]. β zeolite has been reported to be a highly active and selective catalyst for synthesis of ethylamine from ethyl alcohol and ammonia [16]. The formation of amine is reported to occur via intermolecular dehydration of adsorbed alcohol and ammonia.

In the present investigation, the ammonolysis reaction of n-butyl alcohol

is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia. At the reaction conditions employed the alcohol can react either by i) dehydrogenation to form butyraldehyde ii) intramolecular dehydration to form 1-butene or iii) intermolecular dehydrative amination between adsorbed alcohol and ammonia to form n-butylamine [17, 18]. n-butylamine on further alkylation can also yield the secondary and tertiary butylamines. The reaction is investigated to find a catalyst that would give selective production of one of the amines in high yields and at the same time suppress the undesirable formation of dehydrogenation or dehydration products.

Experimental

a. Materials used

Na β , H β were supplied by Sud-Chemie. Zn β was prepared by ion exchange method from Na β with corresponding 0.5 M metal sulphate salt solution.

b. Characterisation

Acidity and Basicity Measurements

Acidity of the catalysts was measured using temperature programmed desorption (TPD) technique using ammonia as a probe molecule in the temperature range of 40 - 480 °C. A known weight of the sample was at first activated in air at 500 °C for 6 hours. The catalyst was then cooled to room

temperature in flowing nitrogen. Anhydrous ammonia was passed over the catalyst for about 30 minutes for adsorption to occur. The sample was then heated at a rate of 5 °C per minute and the amount of ammonia desorbed as a function of temperature was determined. Similarly basicity was measured using CO₂ as a probe molecule.

c. Ammonolysis reaction of n-butyl alcohol:

The ammonolysis reaction of n-butyl alcohol was carried out in a vertical flow type of a reactor system at atmospheric pressure. In a typical experiment, 5 g of the catalyst was packed in a quartz reactor. The catalyst was activated in flowing air for about 6 hours at 500 °C. The temperature was then brought to the reaction temperature in dry nitrogen. n-butyl alcohol (Loba Chemie) and anhydrous ammonia (Bhoruka Gases, 99.8%) were then passed through the reactor, from a syringe feed pump and a gas cylinder respectively at preset flow rates to get the desired alcohol to ammonia ratio and weight hourly space velocity with respect to n-butyl alcohol (LHSV). The reactants were mixed in a pre - heater

cum mixer and then passed over the catalysts. The products were then analysed on a Chemito 8610 HT gas chromatograph using 5" x 1/8" P/W 28 % AT -223 + 4 % KOH on GCR and 5 % SE - 30 column. The liquid products were found to be n-butylamine, dibutylamine, tributylamine, butyraldehyde and butyronitrile and the gaseous product was 1-butene. The reaction was investigated for variations in temperature, LHSV and molar concentrations of mixtures of alcohol and ammonia. In all cases, the results are expressed in terms molar conversion of the alcohol into various products to give a measure of overall catalytic activity. Results are also expressed as percentage molar conversion of alcohol into amines by ignoring the amount converted into the undesirable products viz. butene and butyraldehyde formed by dehydration and dehydrogenation respectively.

Results and discussion

The catalytic activity of different β zeolite catalysts was determined at a preoptimised temperature of 400 °C, LHSV of 1.00 h⁻¹ and molar ratio of alcohol to NH₃ of 1 : 4. The data is shown in Table 1.

Table 1. Catalytic activity of different catalysts for the ammonolysis reaction of n-butyl alcohol.

Catalyst	% conversion of alcohol	% selectivity to products						Total % selectivity to amines	% conversion of alcohol to amines
		Butene	Butyr aldehyde	Butyro nitrile	n- Butyl amine	Dibutyl amine	Tributyl amine		
Na β	41.32	36.83	3.48	1.36	30.08	17.54	10.71	58.33	24.10
H β	58.19	72.30	--	--	16.98	10.72	--	27.70	16.12
Zn β	35.93	77.52	2.95	2.01	10.98	6.54	--	17.52	6.29

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h⁻¹

Molar ratio (alcohol : NH₃) = 1 : 4

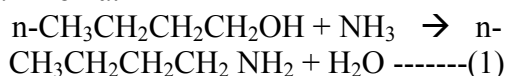
Time on Stream (TOS) = 1 h

All the catalysts showed activity towards formation of amines. It is seen

that H β showed higher conversion than the Na β zeolite. This high conversion

however was mainly dehydration (~ 72 %) to yield butene. H β zeolite also did not show any dehydrogenation activity. On the other hand, Na β zeolite showed a small amount of dehydrogenation activity (~ 5 %) as evident from the formation of butyraldehyde or butyronitrile. In comparison, the dehydration activity of Na β was much lower (~ 36 %). This was accompanied by a high selectivity towards amines (~ 58 %). Also the catalyst Zn β , which showed high dehydration, did not show high selectivity to amines. Therefore, it is believed that the ammonolysis reaction does not take place by addition of ammonia to alkene as a secondary reaction. If it was the case one would have expected selective production of n-butylamine and sec-butylamine, preferably the latter by the expected addition of H-NH₂ to carbon-carbon double bond; but formation of sec-butylamine was also not observed.

Ammonolysis could thus probably occur by direct intermolecular dehydration between alcohol and ammonia.



TPD profiles of adsorbed ammonia (Fig. 1) indicated that no substantial ammonia should be present on the catalysts in adsorbed state at temperatures beyond 300 °C, particularly on the catalysts Na β and Zn β . Hence it is believed that the reaction (1) occurs via Eley-Rideal mechanism involving interaction between gas phase ammonia and adsorbed alcohol. Figure 2 gives TPD profiles of preadsorbed CO₂. The corresponding total acidity and total basicity values are given in Table 2. It is clear from the data in Table 1 that the

highly acidic catalysts give poor conversion and selectivity to amines. It is concluded that low total acidity and high total basicity favours the formation of amines by ammonolysis.

Further optimization of the reaction parameters was carried out to improve selectivity to amines over Na β zeolite catalyst. Table 3 describes the effect of temperature on ammonolysis reaction over Na β .

It can be seen that the percentage conversion increases as the temperature is increased from 350 °C to 480 °C. However at 480 °C, the percentage dehydration was maximum (~ 51 % butene formation). This, as mentioned above is not desirable for getting higher yields of amines. On the other hand, at 450 °C, butene formed was minimum (~ 30 %). As expected, the percentage molar conversion of alcohol to amines was higher (36 %) with ~ 61 % selectivity to amines.

Figure 3 describes this pattern of selectivity to individual amines from the mixture of three amines. It shows that the selectivity to primary amine increases as the temperature is increased. At the same time selectivity to secondary and tertiary amines decreased progressively. This is probably because, at higher temperatures, the primary amine molecules desorb from the catalyst surface at a faster rate thus preventing further alkylation to secondary or tertiary amines. Further investigation of this aspect was carried out by studying the effect of flow rate of reactants at a temperature of 450 °C as shown in Table 4.

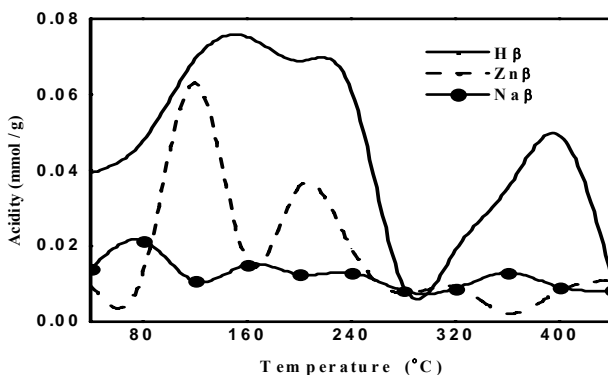


Fig.1. TPD profiles of preadsorbed NH₃ over β zeolite

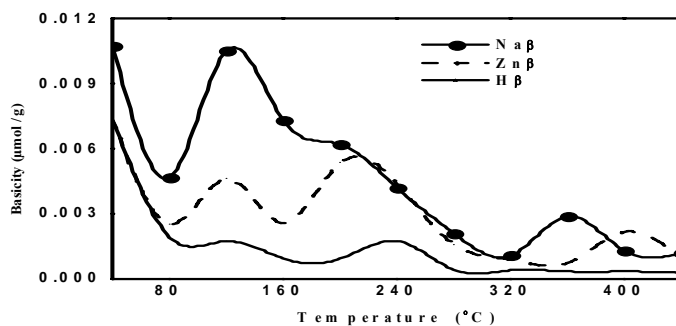


Figure 2. TPD profiles of preadsorbed CO₂ over β zeolites.

Table 2. Total acidity and basicity of β zeolites.

Catalyst	Total acidity (mmol / g)	Total basicity (μmol / g)
Naβ	0.13387	0.05218
Hβ	0.48694	0.01634
Znβ	0.19475	0.03317

Table 3. Effect of temperature on ammonolysis reaction of n-butyl alcohol over Na β zeolite.

Temperature (°C)	% conversion of alcohol	% selectivity to butylamines			Total % selectivity to amines	% conversion of alcohol to amines
		butyl amine	dibutyl amine	tributyl amine		
350	48.16	22.60	18.54	10.99	52.13	25.10
400	51.32	30.08	17.54	10.71	58.33	29.93
450	58.97	36.92	15.13	9.04	61.09	36.02
480	64.16	38.17	6.54	3.91	48.62	31.19

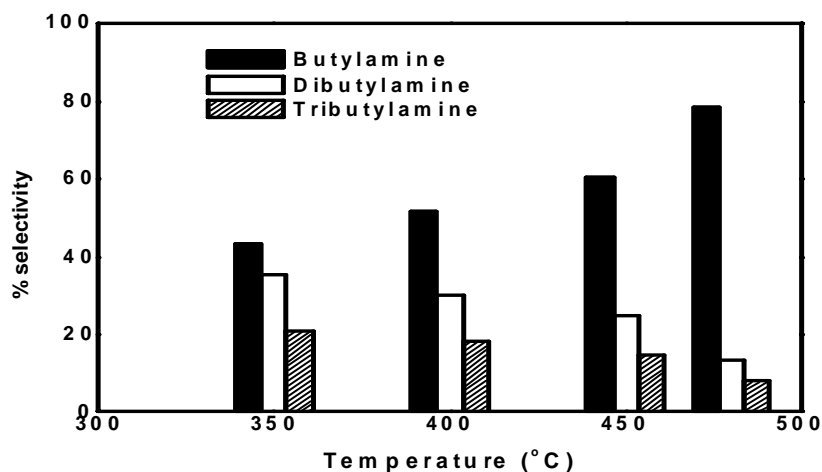
Weight of catalyst = 5 g

LHSV = 1.00 h⁻¹

Molar ratio (alcohol : NH₃) = 1 : 4

TOS = 1 h

Figure 3. Selectivity to individual amines at different temperatures during ammonolysis of n-butyl alcohol over Na β zeolite.



Weight of catalyst = 5 g

LHSV = 1.00 h⁻¹

Molar ratio (alcohol : NH₃) = 1 : 4

TOS = 1 h

Table 4. Effect of LHSV on ammonolysis reaction of n-butyl alcohol over Na β zeolite.

LHSV h ⁻¹	% conversion of alcohol	% selectivity to butylamines			Total % selectivity to amines	% conversion of alcohol to amines
		butyl amine	dibutyl amine	tributyl amine		
0.50	64.07	12.15	20.18	25.05	57.38	36.76
0.75	61.94	8.12	46.13	11.02	65.27	40.42
1.00	58.97	36.92	15.13	9.04	61.09	36.02
1.50	54.32	33.60	11.95	8.62	54.17	29.42
2.00	50.17	34.97	14.36	--	49.33	24.74

Weight of catalyst = 5 g

Molar ratio (alcohol : NH₃) = 1 : 4

It is seen that as LHSV is increased from 0.50 h⁻¹ to 1.0 h⁻¹ the selectivity pattern greatly changes. Thus at the low LHSV of 0.50 h⁻¹ the catalyst is predominantly selective to tributylamine. At 0.75 h⁻¹, large selectivity is observed for dibutylamine (46%) while the selectivity towards tributylamine decreased from 25% to 11%. At still higher LHSV of 1.0 h⁻¹ the catalyst showed selectivity to n-butylamine at the cost of di and tri

Temperature = 450 °C

TOS = 1 h

butylamines. It is thus clear that enhanced alkylation occurs as the initial amine spends longer times on the catalyst surface. Such a process is also known to be a thermodynamically favoured process [19]. Thus, the contact time is one of the key factors for deciding the relative selectivity to different amines.

Further investigation was carried out at various molar ratios of the reactants and the results are presented in Table 5.

Table 5. Effect of molar ratio of reactants on selectivity to amines during ammonolysis reaction of n-butyl alcohol over Naβ zeolite

Molar ratio Alc : NH ₃	% conversion of alcohol	% selectivity to products			Total % selectivity to amines	% conversion of alcohol to amines
		Butyl amine	Dibutyl amine	Tribu tyl amine		
1 : 2	71.06	--	36.48	15.64	52.12	37.03
1 : 3	66.08	1.67	55.43	12.08	69.18	45.71
1 : 4	61.94	8.12	46.13	11.02	65.27	40.42
1 : 5	60.73	42.19	17.48	10.76	70.43	42.77
1 : 6	61.04	54.02	9.68	--	63.70	38.88

Weight of catalyst = 5 g

LHSV = 0.75 h⁻¹

A high conversion ~ 66 % with relatively low butene formation was observed at an alcohol to ammonia molar ratio of 1 : 3. The percentage molar conversion of alcohol to amines was also higher ~ 46 % with predominant selectivity to secondary amine ~ 55 % as compared to a mere < 2 % selectivity to primary amine. As the alcohol to ammonia ratio was increased, the primary amine formation increased to ~ 54 % while the secondary amine formation decreased to a low ~ 10 % at 1

Temperature = 450 °C

TOS = 1 h

: 6 molar ratio of alcohol to ammonia. Thus excess ammonia favoured primary amine formation by preferential interaction of the alcohol with ammonia.

On the other hand when the alcohol to ammonia molar ratio was lowered to 1 : 2, formation of tertiary amine was favoured and no primary amine was detected at this stage. Thus when the concentration of ammonia is low the alcohol instead of undergoing ammonolysis caused further alkylation of the initially formed primary amine.

Thus at an alcohol to ammonia molar ratio of 1 : 3, LHSV of 0.75 h^{-1} at $450 \text{ }^\circ\text{C}$, 45 % of n-butyl alcohol was converted into amines, with greater than 55 % overall selectivity to dibutylamine. Similarly at an alcohol to ammonia molar ratio of 1 : 6, LHSV of 0.75 h^{-1} at $450 \text{ }^\circ\text{C}$, 39 % of n-butyl alcohol was

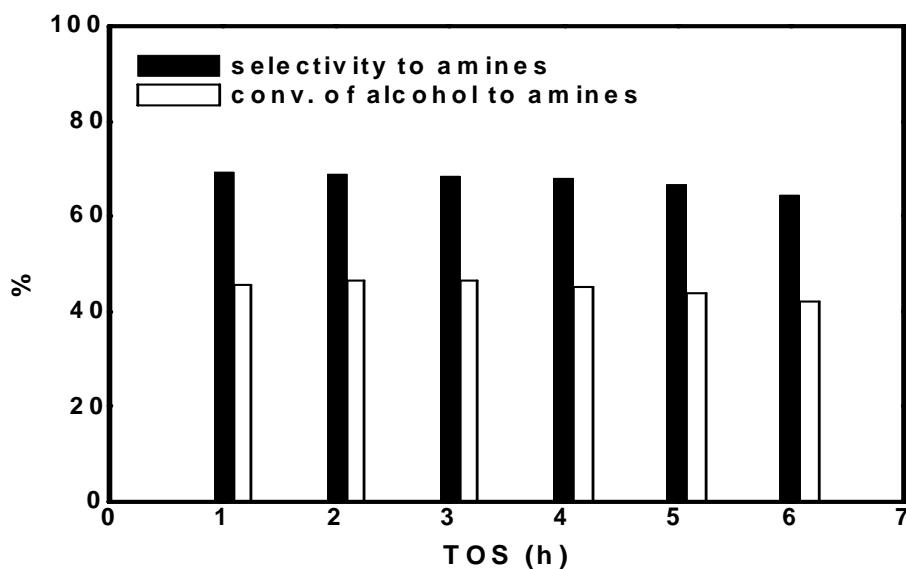
converted into amines with about 54 % selectivity to n-butylamine.

Time on stream (TOS) studies were carried out over Na β zeolite at a temperature of $450 \text{ }^\circ\text{C}$, LHSV of 0.75 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 3. The data is presented in Figure 4.

Figure 4. Time on stream studies over Na β zeolite.

Weight of catalyst = 5 g
LHSV = 0.75 h^{-1}

Temperature = $450 \text{ }^\circ\text{C}$
Molar ratio (alcohol : NH_3) = 1 : 3



The TOS studies show that the activity increases slightly in the second and third hour but then drops a little after 4 hours. Nearly 42 % of alcohol is converted to amines by the sixth hour. Figure 5 shows the pattern of selectivity to individual amine in a mixture of amines at different TOS.

It can be seen from Figure 5 that the primary amine formation drops to zero by the third hour and the selectivity to dibutylamine reaches to about 85 % by the fourth hour. Thus Na β zeolite can be used to obtain dibutylamine with high

selectivity at an optimum conversion of alcohol.

Conclusions

1. β zeolites are investigated as catalysts for the ammonolysis of n-butyl alcohol. The products were mainly primary, secondary and tertiary butylamines.
2. Catalysts H β and Zn β which gave a high dehydration activity, showed a poor activity towards formation of amines.
3. At an alcohol to ammonia molar ratio of 1 : 3, LHSV of 0.75 h^{-1} at $450 \text{ }^\circ\text{C}$, 45 % of n-butyl alcohol was converted into amines, with greater than 55 % overall

selectivity to dibutylamine. When the selectivity amongst the three amines was

considered the proportion of dibutylamine was greater than 85%.

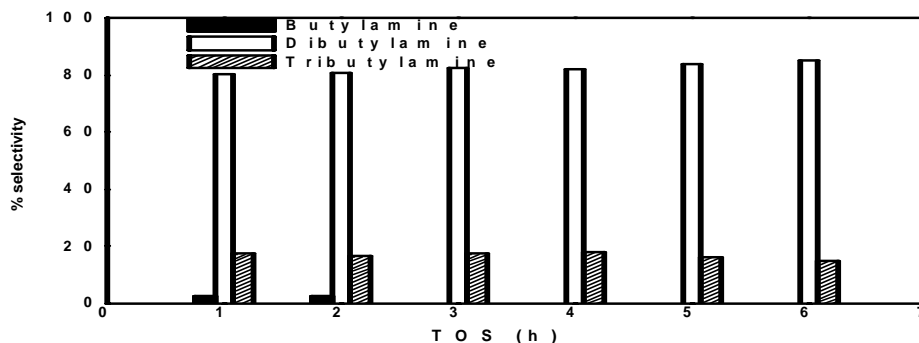


Figure 5. Percentage selectivity to individual amine at different TOS.

Weight of catalyst = 5 g ;
Temperature = 450 °C

LHSV = 0.75 h⁻¹ Molar
ratio (alcohol : NH₃) = 1 : 3

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