Catalysts for Ammonolysis of C_4 Aliphatic Alcohols

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By

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STATEMENT

I hereby declare that the matter embodied in this thesis entitled, "**Catalysts for Ammonolysis of C_4 Aliphatic Alcohols**" is the result of investigations carried out by me in the Department of Chemistry, Goa University, Goa, India, under the supervision of Prof. J. B. Fernandes. In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE

This is to certify that the work entitled, "Catalysts for Ammonolysis of C_4 Aliphatic Alcohols" presented in this thesis has been carried out by Mr. Sachin B. Kakodkar under my supervision and the same has not been submitted elsewhere for the award of a degree.

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Abstract

Ammonolysis is the cleavage of a bond by addition of ammonia. A wide variety of inorganic and organic substrates can be ammonolysed. Aliphatic amines are of considerable importance and find applications in almost every field of modern technology, agriculture and medicine. There are various methods for the synthesis of amines but ammonolysis of alcohols is the most popular method. The ammonolysis reaction is extensively studied for methyl alcohol and ethyl alcohol, however reports on butyl alcohols very few. Also the reported yields for sec- and t- butyl alcohols are low. Zeolites and heteropoly acids are being extensively used in various catalytic applications owing to their acidic properties.

The present investigation deals with the ammonolysis of n-butyl alcohol, sec-butyl alcohol and t-butyl alcohol over ZSM-5, Y, β zeolites and phosphotungstic acid. The zeolites are modified by ion exhange of the cation. Composite catalysts of phosphotungstic acid with zeolites have also been prepared. The catalysts are characterized by X ray diffraction, infrared spectroscopy and BET surface area measurements. Temperature programmed desorption using ammonia and carbon dioxide as probe molecules has been carried out over the catalysts to evaluate the acid and basic sites of the catalyst respectively. The ammonolysis reaction of butyl alcohols is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia over these catalysts. 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 formation of undesirable products.

Main conclusions

- X ray studies revealed that HPWA interacts strongly with zeolite supports in case of both HZSM-5(225) as well as HY zeolite as evident from the additional absorption peaks which are not present in the pure catalysts.
- In the composite catalysts of HPWA and HY, the Keggin structure bands of HPWA grow in intensity as the concentration of HPWA increases from 10 % to 40 % indicating that the bulk properties of HPAs prevail at higher loadings of HPWA on the support.

- Naβ zeolite was found to be highly active catalyst for the selective synthesis of dibutylamine. Highest conversion of alcohol to amines at high selectivity towards dibutylamine (~ 55 %) was observed at a temperature of 450 °C, LHSV of 0.75 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 3 over Naβ zeolite catalyst.
- The catalyst 20%HPWA/HZSM-5(225) was found to be the most active catalyst and showed a high selectivity towards n-butylamine. Highest conversion of alcohol to amines (~ 73 %) was observed at a temperature of 400 °C, LHSV of 1.00 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 5.
- The composite catalyst 20%HPWA/HY was found to be highly active catalyst for the synthesis on sec-butylamine by ammonolysis of sec-butyl alcohol. The catalyst showed ~ 70 % conversion of alcohol to amines with a high selectivity towards n-butylamine at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 6.
- The composite catalyst 30%HPWA/HY was found to be the most active catalyst and showed a high selectivity towards di-sec-butylamine. Highest conversion of alcohol to amines (~ 80 %) was observed at a temperature of 350 °C, LHSV of 0.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4.
- NiZSM-5 zeolite was found to be the most active catalyst for the synthesis of t-butylamine by the ammonolysis of t-butyl alcohol with anhydrous ammonia. Highest conversion of alcohol to amines (~30 %) was obtained at a temperature of 320 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 3
- HZSM-5(40) zeolite was found to be the most active catalyst for the synthesis of t-butylamine by the ammonolysis of t-butyl alcohol with aqueous ammonia.

Chapter 1

Introduction and literature survey

Introduction and literature survey

This Chapter introduces various aspects of ammonolysis, reviews the literature on ammnolysis of alcohols and describes the catalytic systems used in this investigation.

1.1 Introduction to ammonolysis

Ammonolysis is essentially the cleavage of a bond by the addition of ammonia [1].

$$R\text{-}OH + NH_3 \rightarrow R\text{-}NH_2 + H_2O \qquad (1)$$

Ammonolysis always involves replacement of ammonia hydrogen by other atoms or radicals.

$$R\text{-}Cl + H\text{-}NH_2 \rightarrow R\text{-}NH_2 + HCl \qquad (2)$$

Important industrial processes involving ammonolysis are manufacture of urea, melamine, aniline from chlorobenzene, methylamines from methyl alcohol, and ethanolamines from ethylene oxide.

Ammonolysis may involve [2]:

i. *Double decomposition*, in which the NH_3 molecule is split into $-NH_2$ and $-H$ fragments, the former becoming part of the newly formed amine, while the later unites with the radical $-Cl$, $-SO_3H$, $-NO_2$, etc., that is substituted.

ii. *Dehydration*, in which water and amines result from the ammonolysis of either alcohols or phenols and from the hydroammonolysis of carbonyl compounds.

iii. *Simple addition*, in which both fragments of the NH_3 molecule enter the new compound as in the preparation of alkanolamines from alkylene oxides, aminonitriles from unsaturated nitriles and ureas and thioureas from isocyanates and isothiocyanates.

iv. *Multiple activity*, in which nascent or recycled amines compete with ammonia as a co reactant, resulting in the formation of secondary and tertiary amines by aminolysis.

1.1.1 Terms involved in ammonolysis [1]

1. Direct ammonolysis

It involves the reaction of a given substrate with ammonia in the presence or absence of a catalyst at different conditions of temperatures and pressures. Anhydrous NH_3, liquid NH_3, aqueous NH_3 and recently supercritical NH_3 have been used for such processes.

Examples of this type include:

i. Synthesis of primary alkyl amines from alcohols in the presence of dehydrating, hydrogenating / dehydrating catalyst [3 - 9].

ii. Synthesis of nitriles from alcohols in presence of dehydrogenating catalysts [10 - 15].

iii. Direct synthesis of nitriles from hydrocarbons in presence of catalysts [16 - 18].

iv. Catalytic synthesis of amines from alkenes [19 - 21].

v. Synthesis of primary amines from alkyl halides [22 - 24].

2. Aminolysis

It is a reaction, in which, amines play a role analogous to that of NH_3 in ammonolysis. It is often encountered in many instances in which the amines formed by ammonolysis participate in further reactions leading to multiple products. The frequency of such occurrence is enhanced due to kinetic and thermodynamic considerations, which are more favorable to aminolysis than the corresponding ammonolysis.

Examples of such processes include:

i. Synthesis of secondary and tertiary amines by reaction of alcohol and primary amines and secondary amines respectively [25, 26].

ii. Conversion of esters to amides [27 - 33].

iii. Conversion of ethers to amines [34].

iv. Conversion of organic halides to amines [35, 36].

v. Conversion of lactones (propiolactone) to amides or aminoacids [37].

vi. Conversion of acid chlorides to amides [33].

vii. Conversion of aldehydes to azomethines [33] and complex products [38].

viii. Production of substituted ureas from CO_2 [39].

ix. Hydroaminolysis, which is combination of hydrogenation and aminolysis [33, 40, 41].

3. Hydroammonolysis

It is the reaction of a substrate with NH_3 in the presence of hydrogen. The catalysts generally used in these kinds of reactions are hydrogenating catalysts, which are used in combination with either a dehydrogenating or a dehydrating catalyst depending on the organic substrate. It is often termed as ***reductive amination*** when the final product is an amine. It is particularly useful to obtain amines in preference over nitriles in case of alcohols and carbonyl compounds.

Some examples of this type are:

- i. Conversion of alcohol to amines in the presence of hydrogenation / dehydrogenation, hydrogenation / dehydration catalysts [42 - 46].
- ii. Conversion of carbonyl compounds (carboxylic acids, aldehydes and ketones) to amines in the presence of hydrogenation catalysts [47 - 49].
- iii. Conversion of aldoses to amines [50, 51].

4. Indirect ammonolysis

It is a reaction in which substances such as ammonium carbonate or zinc chloride ammoniate [$Zn(NH_3)_2Cl_2$] which decompose with the liberation of ammonia under the reaction conditions are used in place of NH_3 as the ammonolytic reagent.

Examples of this type include:

- i. Reaction of heterocyclic bases with metal amides to give amino derivative [52].
- ii. Manufacture of sulfamic acid from sulphur trioxide by using urea [53].

5. Ammoxidation

It is the reaction of a substrate with NH_3 in presence of air or molecular oxygen generally in presence of a catalyst. In this process, a C-H bond is converted into a C-N bond under oxidative conditions with ammonia. It is often termed as oxidative ammonolysis.

Examples of this type include:

- i. Synthesis of nitriles from alkanes [54 - 57].
- ii. Synthesis of nitriles from alkenes [58, 59].
- iii. Synthesis of nitriles from alcohols [60].

1.1.2 Types of ammonolysis reactions

A wide variety of substances can undergo ammonolysis reactions [1]. Among inorganic compounds, alkali metal hydrides and mono oxides, halides of the lesser electropositive metals and non-metals, and oxides of non-metallic elements may be ammonolysed. In organic compounds, atoms or groups such as hydrogen, hydroxyl, halogen, sulphonic acid groups, certain labile nitro groups, and the oxygen of aldehydes, ketones, certain acids and their derivatives can be replaced by ammonolysis. Ammonolytic cleavage also occurs with acid anhydrides, esters, Schiff's bases, and many organometallic compounds. Ammonolytic addition can take place to double bonds and cyclic structures as in acrylonitrile, lactones, and olefin oxides. Table 1.1 shows a brief overview of various organic substrates, which can be ammonolysed.

Table 1.1 A brief overview of ammonolysis reactions of various organic substrates.

Atoms or groups undergoing ammonolysis	Substrate	Some Examples	Reaction conditions	Remarks	Reference
-H	Hydrocarbons	$C_6H_5CH_3 + NH_3 \rightarrow C_6H_5CN + 3\ H_2$	Dehydrogenating catalysts ~ 525 - 550 °C	Thermodynamically unfavorable at room temperature but favorable above ~ 550 °C	16 - 18
-OH	Alcohols	i) $CH_3OH + NH_3 \rightarrow CH_3NH_2 + (CH_3)_2NH + (CH_3)_3N + H_2O$	~ 450 °C Dehydrating catalysts	a) Hydroxyl replacement thermodynamically favored in liquid state b) Vapour phase ammonolysis favorable at ~ 450 °C c) Combination of ammonolysis and aminolysis	4, 61 - 67
		ii) n-Butanol + $NH_3 \rightarrow$ Butyronitrile	ZnO dehydrogenating catalysts		68, 69
		iii) n-Butanol + $NH_3 \rightarrow$ Butylamines	Dehydrating catalyst		5, 6, 9
		iii) n-Butanol + $NH_3 + H_2 \rightarrow$ Butylamines	Hydrogenation / dehydrogenation, hydrogenation / dehydration catalysts	hydroammonolysis	70 - 72
	Phenols	i) Phenol $\rightarrow$ Aniline	ZSM-5 zeolite	Vapor phase reaction	73

-X (X = F, Cl, Br, I)	Halides	i) Ethylene dichloride → Ethylene diamine	Aqueous NH_3, 100 - 180 °C, under pressure	Mixture of amines obtained	74
		ii) p-Nitrochlorobenzene → p-Nitroaniline	Aqueous NH_3, 175 °C, pressure (no catalyst)	Processes difficult in case of aromatic halides but profitable because of cheap and easy availability of aromatic chlorides	2
		2-Chloroanthraquinone → 2-Aminoanthraquinone	Aqueous NH_3, 200 °C, copper catalyst used to moderate reaction conditions		2
		Chlorobenzene → Aniline	Copper catalyst, 200 – 210 °C, aqueous NH_3		23
		Chloroacetic acid → Glycine	Aqueous NH_3	Mixture of mono-, di- and tri-glycine obtained Use of ammonium carbonate favors glycine formation	75
		o-Dichlorobenzene → o-Phenylenediamines		High quantity of anhydrous NH_3 needed in presence of small quantity of water to obtain satisfactory yields	2

Carbonyl oxygen	Aldehydes	Replacement of carbonyl oxygen by NH_2 group	NH_3 and H_2 needed	Reductions followed by hydroxyl replacement or as ammonia addition followed by reduction Reductive amination or hydroammonolysis (nitiles obtained in absence of hydrogen)	1
		Acetaldehyde → Diethylamine	$NH_3 : H_2$ (1 : 1), Ni - Cr catalyst 120 – 140 °C space velocity = 400 h^{-1}	Primary and tertiary amines obtained as by-products Diethylamine yield (90 – 95 %)	47
		2-Butanone → 2-Aminobutane		Liquid phase reaction	43, 76
		Stearic acid → Stearylamine	Ni-molybdenum sulfide catalyst 300 – 330 °C 200 atm	hydroammonolysis	2
>c=c<	Alkenes	$CH_2{=}CH_2 + NH_3 \rightarrow CH_3\text{-}CH_2\text{-}NH_2$ $CH_3\text{-}CH_2\text{-}NH_2 \rightarrow CH_3CN + 2\ H_2$	~ 540 °C Co / Mn / Cr supported on silica or alumina	Ammonolytic clevage of ethylenic double bond followed by dehydrogenation	77
		Propene → Propionitrile	Co or Ni catalysts 370 °C	Liquid phase operation	78 - 80
		2-Methylpropene → t-Butylamine	Zeolite, heteropoly acids	Gas phase operation	19

CO_2 and CO	CO_2	CO_2 → Urea		Continuous liquid phase ammonolysis under high pressure	81
	CO	Ethylene + CO + NH_3 → Propanamide	230 – 265 °C 500 – 800 atm Cobalt carbonyl catalyst	Direct ammonolysis of CO has no industrial significance	82
-SO_3H and	Sulfonic acid	Anthraquinone sulfonic acid → Aminoanthraquinone			83

1.1.3.1 Thermodynamic aspects of ammonolysis [1]

Replacement of hydroxyl group is the basis of the manufacture of lower alkyl amines from alcohols and ammonia. The free energy change for the reaction,

$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O \qquad (3)$$

is less in the liquid state but more favourable in the vapour phase. The entropy change, although negative, is sufficiently small (- 0.9 cal per degree), such that favourable equilibria can be obtained at temperatures of about 450 °C, over dehydrating catalysts. The free energy change under these conditions is about – 4950 cal mol^{-1}..

The free energy changes for the aminolytic reactions, viz.

$$CH_3NH_2 + CH_3OH \rightarrow (CH_3)_2NH + H_2O \qquad (4)$$

$$(CH_3)_2NH + CH_3OH \rightarrow (CH_3)_3N + H_2O \qquad (5)$$

are still more favourable i.e. - 6520 cal mol^{-1} and – 8400 cal mol^{-1}, respectively, at 450 °C and as these reactions are also affected by catalytic influence, the actual procedure is always a combination of ammonolysis and aminolysis resulting in the production of a mixture of primary, secondary, tertiary amines. The major problem associated with this manufacture is the selection of conditions favourable to obtain optimum yields of the most desirable amine and the development of efficient and economical methods of separating and purifying the products. The free energy changes for hydroxyl replacement are generally favourable in the liquid state and hence liquid phase processes are often utilized preferentially over vapour phase.

Aqueous ammonia is widely used in ammonolytic processes because ammonia is readily handled, stored and recovered in this form. Also higher reaction temperatures can be used under moderate pressures than with anhydrous ammonia in the liquid phase. The presence of water is unavoidable when it is a reaction product and is often found essential for satisfactory operation in some processes. Liquid NH_3, anhydrous NH_3 and recently supercritical NH_3 are also being used for such processes.

1.1.3.2 Thermodynamic comparison of ammonolysis and aminolysis [84]

1. Formation of primary amines

Ammonia undergoes a catalyzed condensation reaction with alcohols (RCH_2OH) to give primary amines according to equation (6)

$$RCH_2OH + NH_3 \rightarrow RCH_2NH_2 + H_2O \text{ ----------- } (6)$$

The reaction involves the cleavage of C-O bond in a primary alcohol and N-H bond in ammonia which has bond enthalpies as 92 and 107 kcal / mol, thus the bond-breaking step requires 199 kcal / mol. The bond making steps involve the formation of a C-N bond in a primary amine, and an O-H bond in water having the respective enthalpies of 82 and 119 kcal / mol. Thus the bond-making steps releases 201 kcal / mol. Within an experimental error, the enthalpies of bond breaking and making steps are equal. In the absence of a significant entropy change therefore, the reaction will be close to being an equilibrium process. The use of dehydration catalysts for these reactions will result in the formation of the amine as water is removed in the equilibrium reaction.

2. Formation of secondary and tertiary amines

Lowered selectivity in the formation of primary amines from the reaction between ammonia and primary alcohols is observed because the product amine undergoes further reaction with the primary alcohol to give secondary and then tertiary amines [equations (7) and (8)].

$$RCH_2NH_2 + RCH_2OH \rightarrow (RCH_2)_2NH + H_2O \text{ --------------- } (7)$$

$$(RCH_2)_2NH + RCH_2OH \rightarrow (RCH_2)_3N + H_2O \text{ -------------- } (8)$$

These transformations can also be brought about by the direct use of a primary or a secondary amine in the reaction with alcohols instead of ammonia. The lowering of selectivity towards the primary amine can be explained based on thermodynamic calculations. In reaction (7), a primary amine is converted into a secondary amine by an alcohol and, in reaction (8); a secondary amine is converted into a tertiary amine by an alcohol. For reaction (7), the respective N-H, C-O, C-N and O-H bond enthalpies are 100, 92, 80 and 119 kcal / mol, thereby making the reaction exothermic by 7 kcal / mol. For reaction (8), the respective bond enthalpies are 92, 92, 72 and 119 kcal / mol, thereby making the reaction exothermic by 7 kcal / mol again.

1.1.4 Kinetics of ammonolysis

The kinetic study of vapor phase ammonolysis of alcohol is complicated because of side reactions that accompany the ammonolysis reaction [2]. Despite the availability of substantial literature reports on operating conditions, effect of flow rates, and the effects of catalysts, there is very less literature on actual mechanism.

A substantial excess of ammonia is generally used in the conversion of reactive organic compounds to amines [83]. Under such conditions, there is no appreciable change in the ammonia concentration of the medium, and the rate expression for the process is pseudo first – order. The energy change for the most amination reactions is favourable at moderate temperatures.

Egly and Smith [85] have studied the effect of operating variables on methylamine production from methanol and ammonia over activated alumina. Nine probable reactions are postulated under commercial operating conditions. These include reactions of methanol with di- and trimethylamines as well as decompositions of the amines. Optimum space velocities were found for a given temperature and pressure at which maximum conversion was obtained. The existence of optimum space velocity has been interpreted qualitatively based on the rates of the various possible reactions. They proposed that trimethylamine in the product can be reduced by adding water to the feed or eliminated by recycling.

There is presently no consensus regarding the mechanism of the amination reaction. Some researchers propose the reaction to be an intermolecular dehydration of the adsorbed alcohol and ammonia occurring on the catalyst surface.

The others propose that the preliminary act of the reaction is dehydrogenation of the alcohol to yield a carbonyl compound, followed by the addition of ammonia to the carbonyl group, to yield imine, and subsequent hydrogenation of the imine to yield amine.

1.1.5 General introduction to amines

Amines are a group of organic compounds, which are derived from ammonia by replacement of one or more hydrogen atoms by organic radicals [83]. Generally, they are bases of widely varying strengths, but few acidic amines are also known.

Amines are classified according to number of hydrogen atoms of ammonia, which are replaced by radicals. Replacement of one hydrogen results in primary amines ($R-NH_2$), replacement of two hydrogen atoms results in secondary amines (R_2NH), and, replacement of all three hydrogen atoms results in tertiary amines (R_3N). The substituent group R may be alkyl, aryl or aralkyl. Another group of amines known as heterocyclic amines are those in which the nitrogen forms a part of ring.

According to Bronsted - Lowry theory of acids and bases, amines are basic because they accept protons from acids. In water, the equilibrium shown in equation (9) lies predominantly to the left.

$$RNH_2 + H_2O \rightarrow RNH_3^+ + OH^- \text{------------------------} (9)$$

The extent to which the amine is successful in picking up a proton from water is given by equation (10), where

$$K_b = [RNH_3]^+ [OH]^- / [RNH_2] \text{------------------} (10)$$

The quantities in bracket signify the concentrations of the species given. For short chain aliphatic amines the basic ionisation constant K_b lies near 10^{-3}, for aromatic amines $K_b < 10^{-9}$; for ammonia $K_b = 1.8 \times 10^{-5}$. Stable salts suitable for the identification of amines are in general formed only with strong acids such as HCl, H_2SO_4, oxalic acid, chloroplatinic acid or picric acid.

Amines constitute an important class of organic compounds. The lone pair of electrons on the amine nitrogen enables amines to participate in a large variety of reactions as a base or a nucleophile. Amines play a prominent role in biochemical systems; they are widely distributed in nature in the form of amino acids, alkaloids and vitamins. Many complex amines have pronounced physiological activity, for example, epinephrine (adrenaline), thiamine or vitamin B_1 and Novocaine. The odour of decaying fish is due to simple amines produced by bacterial action. Amines are used to manufacture many medicinal chemicals such as sulfa drugs and anaesthetics. Aliphatic amines are of considerable industrial importance and find applications in almost every field of modern technology, agriculture and medicine. The aliphatic amines are used in the plastic and protective coat industries as emulsion stabilizers, mold release agents, pigment dispersers and flushing agents. Amines are used as catalysts for polyurethane production and for granular products. Alkyl amines are used as anti-caking and anti-dusting agents. They are used as oxidation inhibitors and catalysts for accelerating vulcanization in the rubber industry. Aliphatic amines find many applications in the petroleum industry, especially as corrosion inhibitors and as components of lubricating oils, greases and fuel oils where they act as sludge dispersants and stabilizers. They are added to gasoline as corrosion inhibitors. Some of the specific applications of $C_1 - C_3$ amines are presented in Table 1.2.

Table 1.2 Important industrial products manufactured using $C_1 - C_3$ amines [1].

Amine	Product	Trade Name	Use
Monomethylamine	1,3 – dimethylxanthine	Theophylline	Antispasmodic
	1-napthyl N-methylcarbamate	Sevin	Insecticide
	N-oleyltaurine	Igepon T	Surfactant
Dimethylamine	Zinc dimethyldithiocarbamate	Ziram	Fungicide
	Dimethylformamide	--------	Solvent
	Dimethylacetamide	--------	Solvent
	1,1 – dimethylhydrazine	UDMH	Propellant
	Dimethylaminoethyl p-butylaminobenzoate	Pontocaine	Anesthetic
	2-(benzhydryloxy)-N,N-dimethylthylamine	Benadryl	Antihistaminic
Trimethylamine	Choline	-------	Catalyst for condensation polymerizations
	Choline chloride	------	Poultry feed
Monoethylamine	2-chloro-4-(ethylamino)-6-(isopropylamine)	Atrizine	Herbicide
	1,3,5 – triazine 2-chloro–4–(1-cyano–1-methyl ethyl amino) 6-ethylamino-1,3,5 -triazine	Cyanazine	Herbicide
Diethylamine	Diethylaminoethanol	--------	Organic intermediate, corrosion inhibitor
	Zinc diethyldithiocarbamate	ethyl ziram	Rubber accelerators
Triethylamine	Triethylammonium phosphate	------	Corrosion inhibitor
Monoisopropylamine	Isopropylamine salt	Glyphosate	Herbicide
Di-n propylamine	N,N-dipropyl-2,6-dinitro 4-trifluromethylaniline	Trifluralin	Herbicide

Uses of butylamines

Butylamines are clear liquids with characteristic ammoniacal odours [1]. Soaps prepared from these amines with fatty acids have high oil to water solubility ratios and are used to form water–in-oil emulsions. Since both butyl- and dibutylamines are generally miscible with hydrocarbons, their soaps are usually soluble in hydrocarbon systems. These solubility and emulsion properties, together with the reactivity, make butyl- and dibutylamine particularly useful in preparing specialty soaps, dyestuffs, rubber chemicals, flotation agents, corrosion inhibitors, petroleum specialties and insecticides. The derivatives of butylamine are widely used as gum inhibitors and anti-oxidants for gasoline, developers for color photography, an oral diabetic drug, and a curing agent for siloxane elastomers. Dibutylamine is used as a corrosion inhibitor and an intermediate for insecticides, pharmaceuticals, floatation reagents, dyestuffs, rubber accelerators of the dithiocarbamate types, and accelerator plasticizers such as dibutylammonium oleate. Tributylamine is used in the manufacture of fungicides. Sec-butylamine is used in the manufacture of pesticides. Di-sec-butylamine is used for the production of herbicides. Tertiary butylamine is used as a chemical intermediate for rubber accelerators, insecticides, fungicides, dyes and pharmaceuticals.

Specific derivatives of butylamines that are of commercial interest include monobutylisocyanate, 1,3-dibutylthiourea and 2-dibutylaminoethanol [86].

1.1.6 Synthesis of amines

Amines are prepared by using a number of methods. Amination of alcohols is however the most popular method for synthesis of amines because of the economic factors. Followings are the important methods of synthesis of amines. The choice of a particular process for the synthesis of amines depends on:

1) the desired amine, 2) the substrate availability and 3) economic considerations.

i. Amination of alcohols with ammonia and amines (primary and secondary) in the presence of hydrogenation – dehydrogenation catalysts

Various catalysts [87] like $CuO\text{-}Al_2O_3$, $Cu\text{-}SiO_2$, etc. have been tried in the temperature range of 220 - 250 °C for the synthesis of both lower as well as higher aliphatic amines.

ii. Amination of alcohols with ammonia or amines

Generally, lower aliphatic amines are synthesised by using this method; the temperature is between 300 to 500 °C, the pressure range is 1 to 200 bar. Suitable catalysts used are alumina [88-90], silica - alumina [90], alumina – magnesia [91] and aluminium phosphate [92]. Japanese workers [93] have applied a series of binary transition metal oxides (TiO_2 - MoO_3, Fe_2O_3 – MoO_3, Cr_2O_3 – MoO_3, Mn_2O_3) with acidic dehydrating function. However, these binary transition metal oxides yielded relatively low selectivities for the desired amines. More recently, zeolites of high silica content (ZSM-5, ZSM-11, ZSM-21) have found applications for the dehydrative amination of alcohols [94]. Depending on molar reactant ratio (alcohol : ammonia), primary, secondary and tertiary amines can be synthesised.

iii. Reductive amination of aldehydes and ketones

Amines are formed from aldehydes or ketones by reaction with ammonia or amines (primary and secondary) and hydrogen in presence of transition metal catalyst e g. nickel [95], platinum [96], palladium or iron [97]. Usually these reactions are performed in the temperature range 120 – 175 °C and at pressure of 5 – 10 bar. Depending upon the molar feed composition, primary, secondary or tertiary amines can be synthesised.

iv. Addition of hydrogen cyanide to branched alkene

Monoamines with tertiary alkyl radicals can be obtained with this method [98]. The reaction is carried out in acidic media with sulphuric acid, acetic acid or dibutyl ether sulfuric acid at temperature of 25 – 50 °C.

v. Other methods

Other less widely used methods of alkylamine preparation are the addition of ammonia to C-C double bond [99], substitution of alkyl halides by ammonia [100], and the catalytic hydrogenation of nitriles [101] and nitroparaffins [102].

The above methods of synthesis of amines are summarized in Table 1.3.

Table 1.3 Important methods for synthesis of alkyl amines.

Method of synthesis	Catalyst	General reaction conditions	Reference
i. Amination of alcohols with ammonia and amines in presence or absence of hydrogen	Al_2O_3, TiO_2 - MoO_3, Fe_2O_3 - MoO_3, Cr_2O_3, ZSM-5, ZSM-11, etc.	200 - 500 °C, 1-200 bar.	87-94
ii. Reductive amination of aldehydes and ketones	Ni, Pd, Pt, Fe, etc.	180 - 200 °C, 5-10 bar	95-97
iii. Addition of hydrogen cyanide to branched alkenes	H_2SO_4, CH_3COOH, etc.	25 – 50 °C	98
iv. Addition of ammonia to alkenes	Co, Mg - SiO_2	350 – 450 °C	99
v. Amination of halogen derivatives	MgO	300 °C	100

1.1.7 Review of ammonolysis / amination of alcohols

Hydroxyl group replacement is the basis of manufacture of lower alkylamines from alcohol and ammonia [1]. The free energy change for the reaction,

$$CH_3OH + NH_3 \rightarrow CH_3NH_2 + H_2O$$

is less in liquid state but more favourable in the vapour phase. Thermodynamic studies show that favourable equilibria are obtained at high operating temperatures (~ 450 °C) over dehydrating catalysts. The free energy change however is more favourable for the aminolytic reactions i. e. formation of secondary and tertiary amines. Hence, the final product is usually a mixture of primary, secondary and tertiary amines. The major problem with the process is the selection of conditions favourable to obtain optimum yields of the most desirable amine and development of efficient and economical methods of separating and purifying the products.

The free energy changes for hydroxyl replacement are more favourable in the liquid state. Hence, liquid state processes are used for manufacture of naphtylamines from naphthols and manufacture of 1,4-diaminoantraquinone from 1,4-dihydroxyantraquinone. However, the lower alkyl amines are usually manufactured in a vapour phase process from the corresponding alcohols. Vapour phase processes are more effective when the reactants and products are sufficiently volatile and resistant to pyrolytic decomposition. The vapour phase ammonolysis can also be combined with other catalytic processes such as hydrogenation and dehydrogenation in order to achieve higher conversions, and especially higher selectivity towards the desired. products. Ammonolytic processes have also been carried out using aqueous ammonia and liquid ammonia. Recently there have been successful attempts to produce amines from alcohols using supercritical ammonia as the ammonolytic reagent [103 - 106].

The lower alkyl amines are usually manufactured in a vapour phase process from the corresponding alcohols through the reaction discovered by Sabatier and Mailhe [107]. Dehydrating catalysts such as alumina [108], aluminum silicate [109] and aluminum phosphate [110 - 112] are used. High molecular weight fatty alcohols with 5 to 18 carbon atoms have been ammonolysed in the vapour phase [90, 113].

The most common example of vapour phase ammonolysis is manufacture of methylamines from methanol and ammonia [114 - 116]. The difficulty associated with this process is the selective production of one of the amines. Hence, it is customary to produce all three amines and then separate them [117, 118]. Egly and Smith [85] have studied the effect of operating variables on methylamine production from methanol and ammonia over activated alumina and proposed nine reactions as probable under commercial operating conditions. These included reaction of methanol with di- and trimethylamines, as well as, decompositions of the amines. Several mechanisms have been suggested for the amination reaction over acidic catalysts involving single acid sites and acid-base pairs [61 - 67, 119]. Higher alkylamines have also been produced by similar procedure from corresponding alcohol and ammonia, the relative proportions of primary, secondary and tertiary amines in most of the cases can be controlled by choosing suitable reaction parameters and by tailoring catalyst properties [117, 118, 120 - 122].

It should be noted that at present there is no consensus regarding the mechanism of the amination reaction. Several workers [123, 124] base their ideas on the assumption that intermolecular dehydration of the adsorbed alcohol and ammonia occurs on the catalyst surface. According to another opinion, the preliminary act of the reaction is dehydrogenation of the original alcohol followed by the addition of ammonia to the carbonyl group and hydrogenation of the resultant intermediate imine to obtain amine [125, 126].

The equilibrium constants and enthalpy of the amination of ethanol, 2-propanol, 1-butanol and 2-butanol have been determined [127]. The equilbrium constants are highest with primary alcohols and disproportionation of primary amines is favoured more in case of amines with non-branched chains. The equation for the kinetics of alcohol amination over an oxide catalyst has been derived based on a constant ratio, and the formulae were verified by the amination of n-decanol [128]. Equations also have been derived for the gas phase catalytic amination of alcohols with amines by the use of variable alcohol - amine ratios [129]. Gumbrin (a clay catalyst that contains 40 % organic material) activated by 30 % H_2SO_4 has been reported for the amination of pentyl alcohol with ammonia at 320 - 400 °C. It was observed that maximum yields of 1-pentylamine were obtained at 340 - 360 °C whereas higher temperatures resulted in increasing dehydration of the alcohol [8].

With increasing molecular weight, additional complications arise such as dehydrogenation to nitriles, dehydration to unsaturated hydrocarbons and molecular rearrangement. However, sometimes these are advantageous as in the production of pyridine from ammonolysis of tetrahydrofurfuryl alcohol [130], cyclization of butyl alcohol [131] and synthesis of heterocycles from ethanol and ammonia over a ZnO / ZSM-5 zeolite hybrid catalyst [132].

The main problem associated with the amination of alcohols is the dehydration and dehydrogenation reactions of alcohols, which reduce the selectivity towards amines. Dehydration can sometimes be suppressed by operating under increased pressures as demonstrated by Kozlov and Akhmetshima [133] in the amination of cyclohexanol with NH_3 over alumina catalyst and by Kozlov and Panova [5] in the amination of isomers of butanol with NH_3 over alumina catalyst. Dehydrogenation to nitriles during the ammonolysis of alcohols may be effectively prevented by the use of hydrogen and hydrogenation catalysts, process being known as hydrommonolysis or reductive amination [1]. Ammonolysis of n-butyl alcohol over pelleted reduced nickel resulted in a considerable amounts of nitrile in the absence of hydrogen whereas the use of hydrogen resulted in a vast suppression of the nitrile product, thereby resulting in a high selectivity towards the amines [43 – 45]. Various catalysts (hydrogenating and dehydrogenating) such as cobalt, chromium, silicon, etc. have been used along with dehydrating catalysts such as alumina, zeolite catalysts.

Fused iron catalysts have been reported for the reaction between alcohols and ammonia in the presence of hydrogen [134 - 135]. High molecular weight secondary alcohols (C_7 to C_{29}) have been converted to the corresponding primary amines by the reductive amination with ammonia over a nickel, cobalt or copper catalyst [136]. Amination of decyl alcohol has been studied over mixed metal oxide catalysts [93]. It is found that the catalytic activity depends on the acid sites of the catalyst. Bassilli and Baiker [137] have studied the amination of 1-methoxy-2-propanol over silica supported nickel catalyst for various parameters. They have concluded that hydrogen is not required as a reactant for the reaction as can be judged by the overall stoichiometry but use of hydrogen proves to be advantageous as it suppresses the disproportionation of amines and also catalyst deactivation. The influence of presence of water in the feed was also studied. It is concluded that the presence of water helps in increasing the conversion of alcohol but results in lowering of selectivity. In addition, the role of ammonia concentration was also studied. It is concluded that ammonia excess helps in increasing selectivity towards primary amine product by suppressing the consecutive reactions that lead to the formation of dialkylated products.

Phenols and cyclic alcohols have also been converted into amines by reaction with ammonia. Aniline has been synthesized from phenol, ammonia and hydrogen over Cu / Al_2O_3 – B_2O_3 [138] and over SiO_2 – B_2O_3 [139]. Sintered iron catalyst has been investigated for the hydroammonolysis of benzyl alcohol with respect to variables such as pressure, temperature and reactant ratio [140]. Dicyclohexylamine is formed by the reaction of phenol with ammonia and hydrogen over a palladium carbon catalyst [141]. Pitale and Rajadhyaksha have studied the amination of phenol [73] with NH_3 over different zeolite catalysts for the formation of aniline. It is found that ZSM-5 zeolite shows a very stable activity compared to zeolite X and zeolite Y and that the reaction rate is controlled by intracrystalline diffusion.

1.1.8 Ammonolysis of butyl alcohols

Although there are numerous reports on the ammonolysis of various alcohols, particularly of methanol and ethanol, there are a very few reports of ammonolysis of butyl alcohols in the literature and patents form a large percentage of such citations.

Al_2O_3 has been used in pure form and in combination with metal oxides such as Fe_2O_3 and TiO_2 in various ratios [6]. Optimum yields (20 – 25 %) of amines were obtained at a temperature of 390 °C and a volume velocity of 0.75 h^{-1} over a catalyst having composition 85 % Al_2O_3 + 15 % Fe_2O_3. Popov [142] has reported amination of various isomeric butyl alcohols over Pt on silica gel and Pt on active carbon. Belov et. al. [143] have studied the amination of n-butyl alcohol with ammonia and hydrogen and observed synergism over NiO - TiO_2 and NiO - SiO_2 catalysts. Kozlov and Panova [5] have studied the amination of isomeric butyl alcohols over activated Al_2O_3 using compressed ammonia (1 - 9 atm NH_3 pressures). They have concluded that pressure increases the yield of amines and decreases that of butylene. Aluminium silicate catalyst [144] has been used for the synthesis of n-butylamines from n-butyl alcohol and ammonia in a fluidized bed reactor. Empirical equations for the design of multitubular reactors, kinetics of ammonolysis and reaction mechanism have been studied. Amination of n-butanol to n-butylamines has been studied in the presence of Raney nickel catalyst using NH_4OH [145]. High selectivity to iso-butylamine has been obtained at a good conversion rate over a Raney nickel catalyst modified with V and Mg for the ammonolysis of iso-butyl alcohol [146]. The modification of the catalyst results in an increased selectivity to secondary amine.

Zeolites have also been used for the amination of butyl alcohols. Hamilton [9] has studied the amination of n-butyl alcohol with ammonia over zeolite catalysts viz. H substituted mordenite, rare earth ion-exchanged X faujasite. It is found that pore size of the zeolite affects the formation of different amines. Thus primary and secondary amines have been prepared in preference to tertiary amines using catalysts having pore size of 5 - 10 Å. Apparently, small pores prevent the passage of tri substituted amine products. Minachev et.al. [7] have studied the amination of n-butyl alcohol with NH_3 a 250 - 450 °C to obtain mixtures of n-butylamines over NaX, NaY and high silica Na zeolites. Faujasites NaX and NaY were the most active catalysts while NaA and Na-mordenite were found to be the least active. The activity of the catalyst was found to increase with the number of delocalised Na^+ cations in the unit cell.

Butylamine and dibutylamine with little or no tertiary amine (tributylamine) has been synthesized by the reductive amination of BuOH using metal exchanged zeolites, which are modified using Co, Ni or Group IA, group IIA or rare earth metals [70]. Cheng et. al. [147] have studied the reaction between n-butyl alcohol and ammonia with respect to dispersion of CuO and NiO on HZSM-5 support by XRD method. It is found that the spontaneous dispersion tendency of CuO is more obvious than that of NiO. The dispersion degrees are different when proportions of CuO and NiO are different. The threshold is 0.12 g CuO / g HZSM-5 that corresponds to optimum proportion of CuO when activity is the maximum for the amination reaction. Amination of sec-butyl alcohol has been carried out in an autoclave using NH_3 and H_2 in the presence of ZrO_2 containing Cu - Cr oxides [148]. Mixture of butylamines is prepared by the amination of butyl alcohol with H_2 and NH_3 in presence of a hydrogenation catalyst Ni/Al_2O_3 [149]. Nitriles are the only product when only dehydrogenating catalyst is used for the ammonolysis of alcohols. Thus, butyronitrile is synthesized by the ammonolysis of butyl alcohol over ZnO [68, 69] and Mo_2N [10].

Table 1.4 Catalysts for ammmonolysis of alcohols.

Catalyst	**Feed composition**	**Reaction conditions**	**Products**	**Reference**
Partially dehydrated aluminium hydroxide	CH_3OH, NH_3	380 °C, 200 atm	MMA, DMA and TMA	150 – 152
$AlPO_4$ / Kaolin X	CH_3OH, NH_3 or MMA	450 - 470 °C	MMA, DMA and TMA	153, 154
Al_2O_3	CH_3OH, NH_3 and steam	450 °C	MMA, DMA	155
SiO_2 - Al_2O_3	CH_3OH, NH_3	300 - 450 °C	MMA, DMA TMA	156
ZSM-5, ZSM-11 and ZSM-21	CH_3OH, NH_3	450 °C	MMA, DMA TMA	157
Zeolite A	CH_3OH, NH_3	300 - 350 °C	DMA	158
Philipsite, FU-1, NU-3, erionite, Chlipoptiolite, Ferrierite, Mordenite, Y	CH_3OH, NH_3	300 - 350 °C	DMA, MMA	159 – 168
Cu – Cr_2O_3	C_2H_5OH, DMA, H_2	180 – 240 °C, 1 – 15 bar	N, N – dimethylethylamine	169
Ni – Re	C_2H_5OH, NH_3, H_2	190 °C, 19 bar	Ethylamine	170
Co - Al_2O_3	C_2H_5OH, NH_3, H_2	170 °C, 16 bar	Ethylamine, diethylamine	171
Co, Ca - Al_2O_3	C_2H_5OH, NH_3, H_2	210 °C, 17bar	Ethylamine	172

Catalyst	**Feed composition**	**Reaction conditions**	**Products**	**Reference**
Hβ, HZSM-5, HY, γ–Al_2O_3	C_2H_5OH, NH_3	410 °C	Ethylamine	173
NaX, NaY	C_2H_5OH, NH_3	55 °C, 18 bar	Ethylamine	174
Ni – Al_2O_3	Isopropanol, NH_3	140 - 150 °C, 4 bar	Isopropylamine	175, 176
Rh(111) or Rh(331)	Butanol, NH_3	240 °C, pressure	Butyronitrile	177
Cu-Ni	dodecyl alcohol, NH_3		dodecylamines	178
Ni	octadecyl alcohol, NH_3		dioctadecylamine	179
iron sulfide	C_2 - C_{12} alcohols, NH_3	445 °C, pressure	C_2 - C_{12} nitriles	180
Cu- Ni - Ru / zeolite	lauryl alcohol, NH_3	150-250 °C, pressure	trilauryllamine	181
Zn - Cr oxide	BuOH, NH_3	340-400 °C	butyronitrile	182
Zn oxide - Th oxide / corundum.	Isobutanol, NH_3		isobutyronitrile	183
Raney Nickel	Me_2CHOH, NH_3	165-215 °C,. 45 - 60 atm	Me_2CHNH_2	184
Ni - Cu - Fe2O3	$H_2NCH_2CH_2OH$, NH_3	180 °C	$H_2NCH_2CH_2NH_2$	185
Ni - Re	$HOCH_2CH_2OH$, NH_3		$HOCH_2CH_2NH_2$, $H_2NCH_2CH_2NH_2$, piperazine	186

Catalyst	Feed composition	Reaction conditions	Products	Reference
Cu - Ni, Cu –Ni - Ba	lauryl alcohol, dimethylamine			187
Ru / ZrO_2	cyclohexanol ,NH_3, H_2		cyclohexylamine	188
10 % Ni / silica catalyst	Ethanol, NH_3			189
Cu-TiO_2	EtOH, Me_2N	220 °C	$EtNMe_2$	190
SAPO- titanium oxide	CH_3OH, NH_3		MMA, DMA, TMA	191
Ni	1,9-nonanediol, H_2, NH_3, H_2O		1,9-diaminononane	192
Cu - Cr / Al_2O_3	BuOH, Me_2NH		N,N-Dimethylbutylamine	193
Metals / Al_2O_3, SiO_2, activated C, kieselguhr, kaolin, and zeolites	BuOH,NH_3	150-300 °C, 0.1 - 5.0 MPa	butylamine	194
ZrO_2 – CuO – CoO - NiO	BuOH, liq. NH_3, H_2	180 °C, 30 bar H	$BuNH_2$, Bu_2NH and Bu_3N	71
Ni - MgO	H_2, NH_3, Me_2CHOH	110 °C	Me_2CHNH_2, $(Me_2CH)_2NH$	195
Cu - Mo, Cu - W	Me_2NH, BuOH, and H	214 °C	Me_2NBu	196
Fe / V_2O_5,	BuOH, NH_3	170 °C	$BuNH_2$, Bu_2NH and Bu_3N	197

Catalyst	Feed composition	Reaction conditions	Products	Reference
Cu - Cr oxides	Me_2CHOH, NH_3	200 °C, 40 atm H	Me_2CHNH_2	198
Cu – Zn - Cr / Al_2O_3	$MeNH_2$ 1-dodecanol, H_2	210 °C	$Me(CH_2)_{11}NHMe$	199
Co	1,3-Propanediol, Sc NH_3		1,3-diaminopropane	103, 106
Co	1,3-cyclohexanediol or 2,4-pentanediol, Sc NH_3		1,3-diaminocyclohexane or 1,3-diaminopentane	104, 105

1.2 Introduction to zeolites as catalytic materials

Zeolites are a class of crystalline aluminosilicates based on rigid atomic framework with well - defined channels and cavities. These cavities contain exchangeable metal cations (Na^+, K^+ etc.) and can hold removable and replaceable guest molecules (water in naturally occurring zeolites). It is their ability to loose water, on heating with a blow torch they hissed and bubbled as though they were boiling and named them "zeolites" from Greek words "zeo" to boil and "lithos" stone.

Zeolites were first described as a mineral group by the Swedish mineralogist Boron and Cronstedt in 1756. For many years, zeolites have been very useful as cation exchangers, as used in water softening, and as molecular sieves for separating molecules of different sizes and shapes. More recently, however, research has been focused on their ability to act as catalysts in a wide variety of reactions. Approximately 40 naturally occurring zeolites have been characterized, but in the quest for new catalysts, more than 160 synthetic structures have been developed.

Zeolites are built of SiO_4 tetrahedra partially substituted by AlO_4 tetrahedra linked to each other by oxygen atoms forming a stable and strongly bonded 3 dimensional framework. These frameworks have definite building units such as chains, rings and regular polyhedra. The structural formula of a zeolite is given by $M_{x/n}[(AlO_2)_x.SiO_2)_y].wH_2O$ where M represents a metal ion with valency n, w is the number of water molecules in the unit cell of zeolites.

The value of the ratio x / y is the characteristic of the structure of zeolite. The sum of x and y (i.e., x + y) represents the total number of tetrahedra.

The industrial use of zeolites as catalysts was started around the year 1960 with the replacement of cracking catalyst based on amorphous aluminosilicate [200 - 203]. Metal-doped Y zeolite proved successful as bifunctional catalysts in the field of hydrocracking [201 - 204]. The discovery of ZSM-5 [205], the first representative of the family of pentasil zeolites [206, 207] was a milestone in zeolite chemistry. The use of silicon-rich pentasil zeolites as acidic, extremely shape selective and heat stable catalysts led to a series of new industrial petrochemical processes [208]. Selectoforming [209], dewaxing [210], olefin oligomeristion [211] and MTG [212, 213] (methanol to gasoline) processes have established themselves as industrial processes alongside cracking and hydrocracking. The combination of acidity and shape selectivity in the zeolite catalysts is an important factor for organic synthesis. The high potential of zeolite catalysts has now been used for specific, highly selective synthesis in the field of intermediates and fine chemicals in recent years [214]. The numerous modifications of zeolites with respect to the number and strength of acid centers, isomorphous substitution [215] and doping with metals provide an opportunity to tailor these catalysts as per the needs of the reactions.

1.2.1 Classification of zeolites

Till to date about 40 natural and more than 160 synthetic zeolites, have been identified. Zeolites are classified based on morphological characteristics [216 - 219], crystal structure [216, 217, 220], chemical composition [216, 217 - 221], effective pore diameter [216, 217, 222], and natural occurrence [216, 217]. Bragg [219] classified the zeolites based on their morphology and which, later on was modified by Meier [218] and Barrer according to the secondary units present in them. Barrer [217] and Sand [221] classified the zeolites based on effective pore diameter into three groups, viz. i. small pore zeolites, ii. medium pore zeolites and iii. large pore zeolites (Table 1.5). Very large pore aluminophosphate molecular sieve (VPI–5) [223] and a gallophosphate molecular sieve (cloverite) [224] have been also discovered. An isomorph of VPI–5 called MCM–9 containing Si atoms has also been reported [225].

Table 1.5 Classification of zeolites based on pore size.

Pore size	Number of tetrahedra	Maximum free diameter
Small	6 and 8	4.3 Å e.g. Erionite
Medium	10	6.3 Å e.g. ZSM-5
Large	12	7.5 Å e.g. zeolite Beta Linde X,Y Mordenite
Extra large pore	18	~ 12 Å e.g VPI -5

1.2.2 Synthesis of zeolites

The crystallisation of zeolites involves first the polymerisation of silicate anions in the solutions mixture which depends on the pH, on the OH^- / H_2O, on the reactant relative concentration, on the stirring, on the temperature, etc. Usually the synthesis is carried out under pressure using autoclaves. Different sizes and morphologies of zeolite grains and a homogenous or heterogenous aluminium distribution along the zeolite framework and along the grains result due to variations in the synthesis conditions like concentrations of reagents, pH, temperature and duration of synthesis. It is observed that catalytic properties, particularly shape selectivity and ageing by coking are greatly influenced by the synthetic procedures. The use of organic cations has opened a new field in the synthesis of new zeolites. These cations are thought to increase the solubility of silicate and the aluminate ions and to arrange the water molecules in template like fashion.

General conditions for zeolite synthesis

The conditions generally used in synthesis are [226]

i. Reactive starting materials such as freshly co - precipitated gels or amorphous solids.

ii. Relatively high pH introduced in form of alkali metal hydroxide or other strong base.

iii. Low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated vapour pressure.

iv. A high degree of super saturation of the components leading to the nucleation of a large number of crystals.

A gel is defined as hydrous metal aluminosilicate which is prepared either from aqueous solutions, reactive solids, colloidal sols, reactive aluminosilicates such as the residue structure of meta- kaolin (derived from kaolin clay by dehydroxylation) and glasses. The gels are crystallized in a closed hydrothermal system at temperatures varying from room temperature to about 175 °C. The time required for crystallization various from a few hours to several days [226].

1.2.3 Structure of zeolites

The fundamental unit in a zeolite is a tetrahedral complex consisting of a small cation such as Si^{+4}, in tetrahedral coordination with four oxygens, the Al^{+3} ion commonly coordinates tetrahedrally with oxygen in silicates. This has profound effect on aluminosilicate structures and their composition. The truncated octahedron or a sodalite unit is the building unit for the commercially important A, X and Y zeolites [227]. In some structures, the tetrahedra link to form infinite chains, which results in fibrous like crystals. In other structures, the tetrahedra are linked in layers or sheets as in mica minerals. If SiO_4 and AlO_4 tetrahedra are linked in three dimensions by a mutual sharing of oxygen alone, a framework structure results. The open framework structure of zeolite gives rise to well-defined pore system extending in 1, 2 or 3 dimensions, which can be intersecting or non - intersecting, linear or non - linear.

1.2.4 Acid sites in zeolites

Substances that can donate protons (H^+) are called Bronsted acids and substances, which can accept an electron pair, are called Lewis acids. Both Bronsted and Lewis acid sites are observed in zeolites. These acidic sites are usually studied by infrared spectroscopic examination of adsorbed molecules [228]. It is important to know the structure, concentration, strength and accessibility of the Bronsted and Lewis acid sites and the details of their interaction with the adsorbed organics.

The Bronsted acidic proton consists of a hydrogen atom bonded to the oxygen atom that connects the tetrahedrally coordinated cations, which form the zeolitic framework. The unique environment of the Bronsted acidic protons in the micropores of zeolites controls the overall behavior of a zeolite to a significant extent. Protons can be incorporated into the zeolite framework by

(a) ion exchange in acid medium if the zeolite is stable under these conditions (high silica zeolites only),

(b) exchange with ammonium ions followed by an activation step whereby ammonia is expelled, and

(c) dehydration of multivalent cation-exchanged zeolites including hydrolysis of the cations.

The Lewis acid centers in zeolites are electron deficient sites (containing an occupied orbital) exhibiting the ability to accept electrons during interaction with molecules. It follows from experimental studies that, in addition to the cationic sites, M^{n+}, AlO^{+} or charged $Al_xO_y^{n+}$ clusters or acceptor sites on tiny oxide particles inside or outside the pore structure formed during pretreatment, activation, reactivation and dehydroxylation of H – forms of zeolites exhibit these properties. Both the Bronsted (OH) and Lewis ($\equiv$ Al) sites are often present simultaneously in the structure at high temperatures.

There are a large number of reactions, which are catalyzed by the acid sites of zeolites. To design and optimize a zeolite catalyst for a specific reaction, the following points are to be considered:

a) the type of acid site needed, Bronsted or Lewis,

b) the acid strength required to activate the reactant molecules, and

c) modifications to maximize the number of the required acid sites in a given zeolite catalyst.

1.2.5 Important features of zeolites

The important structure determining parameters are the Si/Al ratio and the condition of the silicate present in the synthesis mixture [229]. Zeolites are inorganic cation exchangers. Their catalytic activity is usually associated with the presence of acid centers in the intercrystalline surface. In their acid form, the zeolites can be employed without further treatment as catalysts or as carriers for active components. Following are the advantages of zeolite catalysts over conventional acid catalysts.

a. The acid strength and number of acid centers (Bronsted and Lewis acid centers) can be adjusted in a controlled manner during synthesis and or / by subsequent ion exchange. The acid centers can also be arranged regularly within the zeolite skeleton [230].

b. Reactant shape selectivity, product shape selectivity and transition state shape selectivity can be obtained with zeolite catalysts which results in highly selective synthesis which is highly advantageous in fine chemical synthesis and various industrial processes [231].

1.2.6 Important applications of zeolites

a) The most important application of zeolites is in reactions catalyzed by Bronsted and Lewis acids, where the change from a homogeneous to a heterogeneous procedure brings an advantage with respect to easy separation and disposal of the catalyst, avoidance of corrosion etc.,. In this regard their shape selectivity has an advantageous effect on the composition of the products, e.g. on the preferred selectivity for the p-isomer in isomerization reactions of aromatic compounds.

b) Zeolites make it possible to increase the activity and stability of the catalysts towards steam and high temperature treatment whenever they are used as support materials. Doping with suitable metals enables hydrogenation and oxidation reactions to be easily carried out. In all these cases, the shape selectivity of the zeolite support is an additional factor controlling the reaction. The introduction of the active components can be carried out by ion exchange or by impregnation. In these cases the acid H-form of the zeolite (HY, HZSM-5, etc.) is converted, for example, into the doped form (CeY, PdZSM-5, etc.)

c) The high thermal stability of the zeolites permits them to be used at high reaction temperatures. They are, therefore, advantageous for reactions in which the thermodynamic equilibrium requires high temperatures. Also high reaction temperatures help in recovering process heat effectively.

d) Zeolite catalysts can be regenerated readily with air merely by burning off the coke, which is frequently responsible for their deactivation. After this treatment, the catalyst generally regains their initial activity enabling them to have a comparatively higher lifetime.

1.3 Heteropoly acids as catalytic materials

1.3.1 Introduction

These are compounds in which one atom of elements such as P, Si, As, B, Al, etc., is combined with a relatively large number of atoms of an element such as W or Mo together with a large number of atoms of oxygen. They form crystals of a complex structure containing large amounts of water of crystallization. They also form insoluble crystalline precipitates with substances having large molecules. Heteropoly compounds provide a good basis for the molecular design of mixed oxide catalysts and possess a high capability as catalysts. This is because the relationships among the following four levels of information can be established on the molecular basis: (i) catalytic performance, (ii) chemical and physical property, (iii) molecular and bulk composition and structure, and, (iv) method of synthesis of catalyst [232 - 236]. The catalytic function of heteropoly compounds has attracted much attention in recent times. Their variety and high potential as catalyst makes this class of compounds very attractive. They are used in solution as well as in the solid state as acid and oxidation catalysts. Merits of solid heteropoly catalysts for catalyst design at the atomic / molecular level are:

1. Systematic variations of acid and redox properties are possible for catalyst design.
2. Molecular nature of solid heteropoly compounds originating from heteropolyanion molecules enables precise design of catalysts and molecular description of catalytic processes.
3. A variety of reaction fields are available for catalytic systems.
4. The unique basicity of polyanions.

Research in heterogeneous catalysis has revealed the presence of quantitative relationships between the acid or redox properties and catalytic performance of heteropoly catalysts, as well as, their unique behavior in heterogeneous catalysis such as pseudoliquid-phase (bulk-type (I)) and the bulk-type (II) catalysis [232 - 242]. Several industrial processes have been utilizing heteropoly compounds as catalysts [232, 243]. In addition, many known and new heteropoly compounds are being applied to a wide variety of reactions. The research activity in heteropoly acid catalysis is very high and growing rapidly.

1.3.2 Structure and properties of heteropoly compounds in the solid state

1.3.2.1 Primary, secondary, and tertiary Structures

HPAs in the solid state are ionic crystals (sometimes amorphous) consisting of large polyanions (primary structure), cations, water of crystallization, and other molecules. This three-dimensional arrangement is the "secondary structure". The tertiary structure is the structure of solid HPAs as assembled. The size of the particles, pore structure, distribution of protons in the particle, etc., are the elements of the tertiary structure. The catalytic function of solid HPAs is highly dependent on the tertiary structure [232, 233].1.3.2.2 Thermal Stability

There are various kinds of stabilities, for example, thermal stability and hydrolytic stability in solution. These stabilities vary depending on the kind of HPAs [232, 236]. Some solid HPAs are thermally stable and applicable to vapour phase reactions carried out at high temperatures. The thermal stability of hydrogen forms of HPAs changes with heteroatom, polyatom, and polyanion structure as follows: $H_3PW_{12}O_{40}$ > $H_3PMo_{12}O_{40}$ > $H_4SiMo_{12}O_{40}$. $H_3PW_{12}O_{40}$ is much more stable than

$H_6P_2W_{18}O_{62}$ [244 – 246]. ^{31}P NMR and thermoanalysis studies have shown that thermolysis of $H_3PMo_{12}O_{40}$ proceeds by losses of water of crystallization and subsequently constitutional water to form $PMo_{12}O_{38}$ [247]. Above 723 K, the Keggin structure of $H_3PMo_{12}O_{40}$ is destroyed.

1.3.2.3 Adsorption and Absorption Properties

Some solid HPAs (group A, hydrogen forms included) absorb a large quantity of polar or basic molecules such as alcohols and nitrogen bases in the solid bulk [235, 248, 249]. The absorption capacity largely depends on basicity and the size of the molecule to be absorbed and the rigidness of the secondary structure. As for desorption, alcohols absorbed can readily leave the bulk, but desorption of pyridine and ammonia needs a high temperature. Nonpolar molecules like hydrocarbons are usually adsorbed only on the surface of group A and B salts. Diffusion coefficients for $H_3PW_{12}O_{40}$ are found to be much lower than those in the micropores of zeolites but are close to those in the liquid phase [248 -250]. The quantity of the absorbed molecules is usually found to be integral multiples of the number of protons [248, 249]. The rigidness of HPAs depends on the countercations (size, charge, etc.) as well as on the water content.

1.3.2.4 Acidic Properties

In early studies, it was shown that HPAs such as $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ in the solid state are pure Bronsted acids [251] and stronger acids than the conventional solid acids such as SiO_2-Al_2O_3, H_3PO_4/SiO_2, and HX and HY zeolites [252, 253]. Hammett indicators test has suggested $H_3PW_{12}O_{40}$ to be a superacid [253 – 256], although firm evidence has not been established. According to a report pyridine adsorbed on $H_3PW_{12}O_{40}$ mostly remains at 300 °C, whereas pyridine adsorbed on SiO_2 - Al_2O_3 is completely desorbed at 300 °C, which indicates that $H_3PW_{12}O_{40}$ is a very strong acid [248]. Thermal desorption studies of ammonia has shown $H_3PW_{12}O_{40}$ to be a stronger acid than ZSM-5, but weaker than SO_4^{2-}/ZrO_2 [254]. The acid strengths of heteropolytungstic acids determined quantitatively by calorimetry of ammonia absorption [252, 257] showed that the acid sites of $H_3PW_{12}O_{40}$ are rather uniform and more strongly acidic than the acid sites of HZSM-5 zeolite. Calorimetric titrations carried out in acetonitrile have indicated that anhydrous $H_3PW_{12}O_{40}$ is a superacid [258]. The strength and the number of acid centers of HPAs can be controlled by the structure and composition of heteropolyanions, the extent of hydration, the type of support, the thermal pretreatment, etc.

1.3.3 HPAs supported on high surface area supports

Dispersing HPAs on solid supports with high surface areas is often important for catalytic applications because the surface area of unsupported HPAs is usually low (1-15 m^2 / g). The supported catalysts have been characterized by various methods and the changes in the acid strength, redox properties, and structures have been reported. In general, HPAs strongly interact with supports at low loading levels, while the bulk properties of HPAs prevail at high loading levels. Acidic or neutral substances such as SiO_2, active carbon, acidic ion-exchange resin are suitable supports, the most frequently used support being SiO_2 [232, 233, 235]. Solids having basicity such as Al_2O_3 and MgO tend to decompose HPAs [259 - 262]. Certain active carbons can firmly entrap HPAs and, therefore, show high stability against the leakage into solvent from the carrier, when HPAs are used in solution [263 - 265]. The maximum loading level of HPAs on carbons was ~ 7-14 wt % and varied moderately with the physical properties of the carbon support, but little with the chemical treatment [239]. HPAs supported on Amberlyst-15, a strongly acidic ion-exchange resin, were found to exhibit enhanced catalytic activity reaction of acrylnitrile and N-adamantanol to form N-adamantylacrylamide [266, 267]. The activity was much higher than those of Amberlyst-15 and that of the acids supported on active carbon. The higher activity of HPAs supported on Amberlyst-15 was explained based on synergism due to the interaction of the heteropolyanions and protons of the ion exchanger. Microcalorimetry of ammonia adsorption has shown that $H_3PW_{12}O_{40}$ suppoted on SiO_2 resulted in a decrease in the acid strength. Only 20 % of the entire protons remained as strong as the ones in the neat $H_3PW_{12}O_{40}$, and the rest showed heats of adsorption similar to those of HX and HY zeolites [264]. It was reported that the acid strength of supported $H_3PW_{12}O_{40}$ diminished in the following sequence of supports: SiO_2 > Al_2O_3 > activated charcoal [257]. The interactions between $H_3PW_{12}O_{40}$ and the surface OH groups of SiO_2 have been detected at low loading levels by ^1H and ^{31}P MAS NMR and Raman spectroscopies [268 - 272]. Heteropolymolybdates such as $H_4SiMo_{12}O_{40}$, $H_3PMo_{12}O_{40}$, and $H_5PMo_{10}V_2O_{40}$ supported on SiO_2 mostly retain the Keggin structure at a high loading level, but partly decompose at very low loading due to their strong interactions with surface silanol groups [273 - 278]. A thermally decomposed Keggin structure on SiO_2 surface can be reconstructed in some cases upon exposure to water vapour [273, 279]. P in $H_3PW_{12}O_{40}$ supported on SiO_2 is reported to be partially replaced with Si of the support [280]. Thus, heteropolyanions on the oxide surface show dynamic behavior depending on the nature of the support and loading levels. $H_3PW_{12}O_{40}$ supported on mesoporous pure-silica molecular sieve MCM-41 and pillared layered double hydroxide exchanged with Keggin heteropolyanions has been reported [281]. It is shown that $H_3PW_{12}O_{40}$ retains the Keggin structure at loading levels above 20 wt % on MCM-41. However, no crystalline phase of $H_3PW_{12}O_{40}$ is seen at loading levels as high as 50-weight %.

1.3.4 HPAs in heterogeneous catalysis

1.3.4.1 Three Types of Catalysis

There are three types of catalysis of solid HPAs; (1) surface, (2) bulk type I (pseudoliquid), and (3) bulk type II catalysis. The latter two were demonstrated for a long period specifically for heteropoly catalysts, but were found applicable for other solid catalysts, as well.

1. Surface-Type Catalysis

Surface-type catalysis is the ordinary heterogeneous catalysis, where the reactions take place on the two-dimensional surface (outer surface and pore wall) of solid catalysts. The reaction rate is directly proportional to the surface area in principle.

2. Bulk-Type (I) Catalysis

In the bulk-type (I) catalysis, the reactant molecules are absorbed in the interpolyanion space of the ionic crystal. The molecules undergo reaction there, and then the products desorb from the solid [236, 248, 249]. The solid in a sense behaves like a solution and the reaction field becomes three-dimensional. Therefore, it is often called as pseudoliquid catalysis. The reaction rate is found to be proportional to the volume of catalyst in the ideal case. For example, the rate of an acid-catalyzed reaction is governed by the bulk acidity. This type of catalysis has been observed for gas-solid as well as liquid-solid systems [282].

3. Bulk-Type (II) Catalysis

Certain oxidation reactions like oxidative dehydrogenation and oxidation of hydrogen at high temperatures exhibit bulk-type (II) catalysis [283]. In this type of catalytic oxidation, although the principal reaction may proceed on the surface, the completely solid bulk takes part in redox catalysis owing to the rapid migration of redox carriers such as protons and electrons. The rate is proportional to the volume of catalyst in the ideal bulk-type (II) catalysis.

1.3.4.2 Heterogeneous Acid-Catalyzed Reactions

Acidity, basicity, and pseudoliquid behavior are the factors governing the acid catalysis of solid HPAs. The acidic properties are mainly controlled by the following factors

(i) the structure and composition of the heteropolyanion,

(ii) the countercations, and

(iii) the dispersion on supports.

The acid strength is mainly controlled by factor (i), and the number of acid sites is greatly influenced by factors (ii) and (iii). The secondary and tertiary structures are also affected by the above three factors. Apart from the acidic properties, the absorption properties for polar molecules are critical in determining the catalytic function in the case of pseudoliquid catalysis. Soft basicity of the heteropolyanion sometimes plays an important role for high catalytic activity in the liquid phase. The acidity of hydrogen forms in the solid state is reflected in the acidity in solution. The acid strength decreases when Mo replaces W and when Si replaces the central P atom for Keggin HPAs. On the other hand, for HPAs of Mo it has ben reported that the acid strength in solution is not correlated with that in the solid state [284]. The catalyst deactivation is usually observed during the course of a catalytic reaction, and the deactivation is sensitive to the kind of reactant, product, solvent, and reaction temperature. The possible causes for the catalyst deactivation could be coke formation, adsorption of products, catalyst reduction, catalyst decomposition and catalyst dissolution. The catalyst deactivation can be avoided by selecting a catalyst having uniform and appropriate acid strength.

Table 1.6 Acid-catalyzed reactions with solid heteropoly compounds [285].

Reaction	Catalyst
$RCO_2H + R'OH \rightarrow RCO_2R$	$H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$/MCM-41
Alkylation of alkylphenol by isobutylene (shape selective)	$H_3PW_{12}O_{40}$/MCM-41
Trioxane + phenol	Silica-included $H_3PW_{12}O_{40}$
Isobutane + n-butenes → C_8 alkylates	$H_3PW_{12}O_{40}$/MCM-41 $K_{2.6}H_{0.4}PW_{12}O_{40}$ (supercritical)
Diels–Alder reaction of quinone	$H_3PW_{12}O_{40}$
Acylation of xylene	$Cs_2HPW_{12}O_{40}$
Adamantylamide synthesis	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
Hydration of dimethylbutene	$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
Ethyl acetate from acetic acid	HPA (commercialized)
Michael addition (pseudoliquid)	$H_3PW_{12}O_{40}$

1.4 Catalysts used in the present investigation

1.4.1 ZSM-5 zeolite

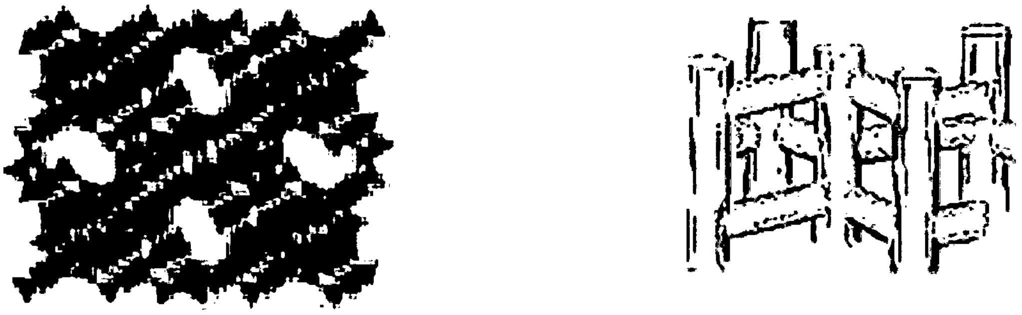

Figure 1.1 Structure of ZSM-5 zeolite.

ZSM-5 zeolite was first synthesised by Mobil Oil Corporation in 1972. It has a MFI topology with a 10 membered ring forming channels intersecting at right angles with sinusoidal channels. It possesses an orthorhombic lattice with 12 distinct T sites. The Si/Al ranges from 10 to Infinity. A structure-directing agent is needed for the synthesis.

1.4.2 Y zeolite

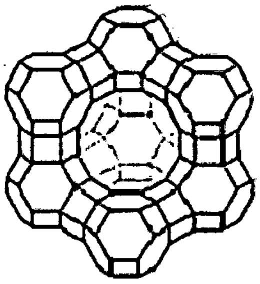

Figure 1.2 Structure of Y zeolite.

Y zeolite was first synthesised by Union Carbide in 1964. It possesses faujasite morphology with 12 membered rings forming a three-dimensional pore system. It has a cubic lattice having only one T site. It is less siliceous (Si/Al = 1 to

25) compared to ZSM-5 zeolite. Hence, there is no need for an organic template during synthesis because of high Al content.

1.4.3 β zeolite

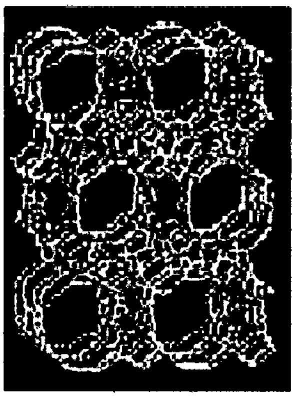

Figure 1.3 Structure of β zeolite.

β zeolite was first synthesised by Mobil Oil Corporation in 1967. It has BEA morphology with a three-dimensional pore system of 12 membered rings. It possesses a tetragonal lattice with 9 distinct T sites. The Si/Al ratio ranges from 10 to infinity. Hence a structure-directing agent is needed during synthesis. It has the same use as ZSM-5 zeolite but has a larger pore system.

1.4.4 Phosphotungstic acid

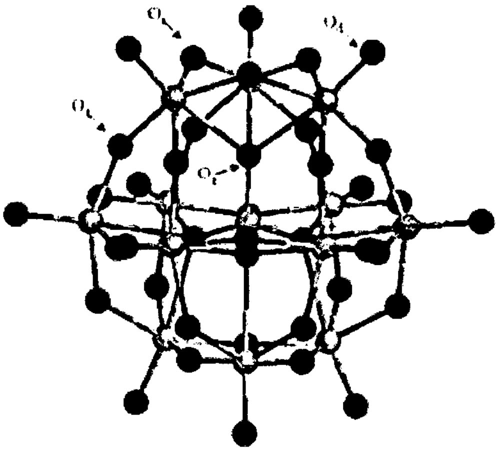

Figure 1.4 Structure of phosphotungstic acid.

Phosphotungstic acid is the strongest acid of the heteropoly acids .The heteropolyanion represents the primary structure of phosphotungstic acid, which then forms a bulk structure by coordinating to acidic protons or other cations. A relatively stable form of phosphotungstic acid contains 6 water molecules per Keggin unit and forms a body centered cubic structure.

Chapter 2

Experimental

Experimental

This Chapter describes the preparation and the characterisation of the catalysts used in this investigation.

2.1 Preparation of catalysts

The catalysts used for the studies are listed in Table 2.1.

Table 2.1 Catalysts and their source.

Catalyst	Source
HZSM-5(40)	Sud Chemie, India
HZSM-5(80)	Sud Chemie, India
HZSM-5(225)	Sud Chemie, India
NaZSM-5 (Si/Al =40)	Sud Chemie, India
CuZSM-5	Prepared by ion exchange with NaZSM-5
NiZSM-5	Prepared by ion exchange with NaZSM-5
ZnZSM-5	Prepared by ion exchange with NaZSM-5
NaY	Sud Chemie, India
HY	Prepared by ion exchange with NaY
CuY	Prepared by ion exchange with NaY
NiY	Prepared by ion exchange with NaY
ZnY	Prepared by ion exchange with NaY
Naβ	Sud Chemie, India
Hβ	Sud Chemie, India
Cuβ	Prepared by ion exchange with Naβ
Niβ	Prepared by ion exchange with Naβ
Znβ	Prepared by ion exchange with Naβ
Phosphotungstic acid (HPWA)	Loba Chemie, India (extra pure)
20%HPWA/HZSM-5(225)	Prepared by mechanical mixing of HPWA and HZSM-5(225)
20%HPWA/NiZSM-5	Prepared by mechanical mixing of HPWA and NiZSM-5
10%HPWA/HY	Prepared by mechanical mixing of HPWA and HY
20%HPWA/HY	Prepared by mechanical mixing of HPWA and HY
30%HPWA/HY	Prepared by mechanical mixing of HPWA and HY
40%HPWA/HY	Prepared by mechanical mixing of HPWA and HY
NiZSM-5(225) (Si/Al =225)	Prepared by ion exchange with HZSM-5(225)

2.1.1 Ion exchange of zeolite catalysts

The ion exchange of zeolite catalysts was carried out by reflux method. To optimise the conditions for ion exchange, the ion exchange of copper with NaZSM-5 and NaY zeolite was carried out using aqueous solutions of copper sulphate pentahydrate ($CuSO_4.5H_2O$) of different concentrations viz. 0.25 M, 0.50 M, 1.00 M and 1.50 M. 1000 mL of copper sulphate solution was refluxed with 8 g of the zeolite for about 18 hours in all cases. The solution was then filtered and washed well with hot water until free of sulphate ions. The residue was dried at 120 °C for about 5 hours and then finely powdered in a mortar and pestle. The extent of ion exchange in each case was evaluated by titrimetry. Table 2.2 gives the amounts of copper ions exchanged with NaZSM-5 and NaY zeolite.

Table 2.2 Extent of Cu^{+2} ion exchange with NaZSM-5 and NaY zeolite.

Catalyst	Percentage of copper ions exchanged with different concentrations of $CuSO_4.5H_2O$			
	0.25 M	0.50 M	1.00 M	1.50 M
CuZSM-5	1.34	1.42	1.38	1.29
CuY	4.65	4.52	4.32	4.62

It was observed that the extent of ion exchange with different concentrations was nearly equal. Hence for the preparation of copper, nickel and zinc ion exchanged zeolites from the sodium from i.e. from NaZSM-5, NaY and Naβ zeolite respectively; 0.5 M solutions were used for ion exchange. 1000 mL of 0.5 M solutions of corresponding metal ion sulphate salt was refluxed with 8 g of the zeolite for about 18 hours. The solution was then filtered and washed well with hot water until free of sulphate ions. The residue was dried at 120 °C for about 5 hours and then finely powdered in a mortar and pestle. The extent of ion exchange in each case was determined by titrimetry. In certain cases, the reflux was carried out twice to check whether the extent of ion exchange showed a significant difference after the second refluxing. However, it was observed that there was no significant difference in exchange levels after refluxing for a second time.

Table 2.3 shows the percentage of respective metal ion exchange levels in case various zeolites.

Table 2.3 Extent of ion exchange of metal ions with zeolite catalysts using 0.5 M aqueous solution of salts of metal sulphates.

Catalyst	% Metal ion exchange
CuZSM-5	1.42
NiZSM-5	1.37
ZnZSM-5	1.49
NiZSM-5(225)	0.62
CuY	4.52
NiY	4.64
ZnY	4.45
Cuβ	2.34
Niβ	2.41
Znβ	2.38

HY was prepared from NaY zeolite by ion exchange by reflux method. 10 g of NaY zeolite was refluxed with 1000 mL of 1 M NH_4NO_3 solution for 16 hours. The solution was filtered to obtain NH_4Y zeolite, which was dried at 120 °C for about 5 hours and again refluxed with another 1000 mL of 1M NH_4NO_3 solution for 16 hours. The contents of the flask were filtered and dried at 120 °C for about 5 hours. NH_4Y zeolite thus obtained was calcined in air at 550 °C in a muffle furnace for 16 hours to obtain HY zeolite.

2.1.2 Preparation of composite catalysts

The various composite catalysts were prepared by a thorough mechanical mixing of the individual catalysts in stoichiometric quantities for 16 hours. Table 2.4 gives the amounts of individual catalysts used to prepare the compsite catalysts.

Table 2.4 Preparation of different HPWA/zeolite composite catalyst formulations.

Catalyst	Weight of HPWA taken (g)	Weight of zeolite taken (g)
20%HPWA/HZSM-5(225)	2	8
20%HPWA/NiZSM-5	2	8
10%HPWA/HY	1	9
20%HPWA/HY	2	8
30%HPWA/HY	3	7
40%HPWA/HY	4	6

2.2 Characterisation of catalysts

2.2.1 X ray diffraction

X ray diffraction studies were carried out on an ITAL STRUCTURES APD2000 X ray diffractometer. The samples were scanned in a 2θ range of 5^0 to 50^0 using Ni filtered CuK_α radiation of wavelength 1.54 nm.

Figure 2.1 to Figure 2.5 show the XRD profiles of various catalysts and the corresponding XRD data is presented in Table 2.5 to Table 2.9.

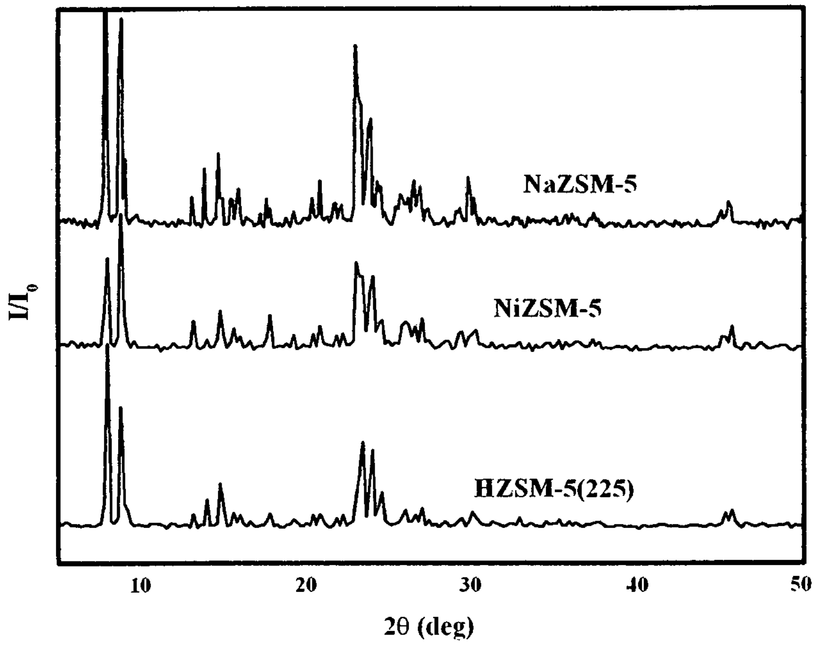

Figure 2.1 XRD profiles of ZSM-5 zeolite catalysts.

Table 2.5 XRD data of ZSM-5 zeolite catalysts.

NaZSM-5		NiZSM-5		HZSM-5(225)	
d (Å)	I/Io	d (Å)	I/Io	d (Å)	I/Io
11.05	100	11.05	68	11.05	100
10.00	50	10.00	100	10.00	60
6.70	8	6.70	23	6.70	--
6.37	13	6.37	--	6.37	--
5.97	17	5.97	30	5.97	24
4.90	6	4.90	27	4.90	8
4.25	10	4.25	19	4.25	2
3.85	34	3.85	54	3.85	47
3.71	30	3.71	50	3.71	40
3.62	11	3.62	27	3.62	25
3.43	8	3.43	22	3.43	10
3.30	12	3.30	24	3.30	11
3.05	12	3.05	8	3.05	2
2.98	4	2.98	10	2.98	9
2.00	5	2.00	6	2.00	4

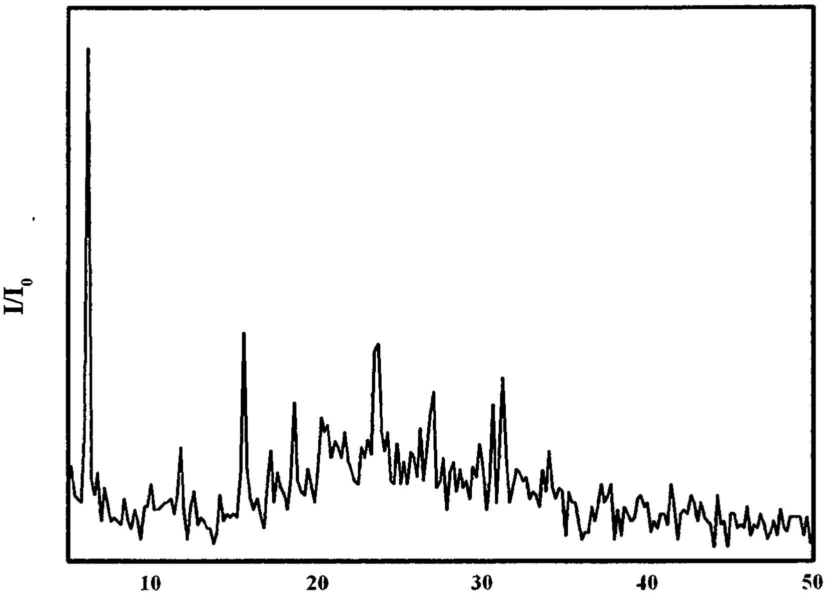

Figure 2.2 XRD profile of HY zeolite catalyst.

Table 2.6 XRD data of HY zeolite catalyst.

HY	
d (Å)	I/I0
14.24	100
8.83	15
7.49	22
5.68	45
5.15	22
4.76	31
4.34	25
3.79	42
3.30	40
2.99	23
2.86	36
2.63	22
2.41	15
2.17	15

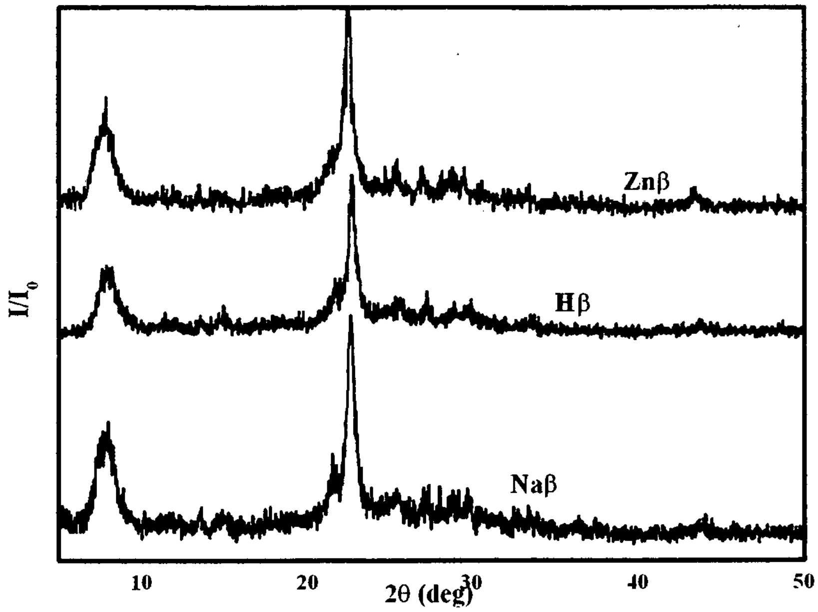

Figure 2.3 XRD profiles of β zeolite catalysts.

Table 2.7 XRD data of β zeolite catalysts.

Naβ		Hβ		Znβ	
d (Å)	I/I0	d (Å)	I/I0	d (Å)	I/I0
16.90	18	16.90	--	16.90	--
14.96	--	14.96	--	14.96	28
13.48	--	13.48	10	13.48	--
12.75	24	12.75	--	12.75	--
12.10	--	12.10	30	12.10	--
11.04	54	11.04	48	11.04	62
10.77	--	10.77	47	10.77	38
9.68	--	9.68	22	9.68	--
6.55	14	6.55	16	6.55	15
5.55	13	5.55	23	5.55	14
5.08	16	5.08	--	5.08	--
4.99	17	4.99	18	4.99	--
4.29	19	4.29	40	4.29	35
3.93	100	3.93	100	3.93	100
3.66	--	3.66	24	3.66	--
3.29	26	3.29	32	3.29	--
3.17	27	3.17	30	3.17	19
3.00	25	3.00	--	3.00	23
2.75	17	2.75	--	2.75	--
2.68	18	2.68	16	2.68	16
2.46	13	2.46	8	2.46	13
2.11	13	2.11	15	2.11	14

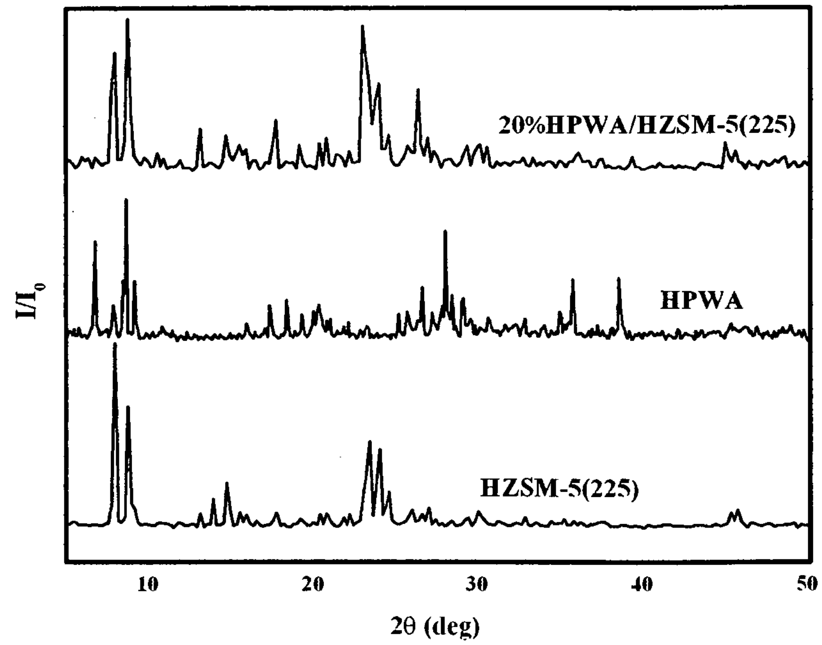

Figure 2.4 XRD profiles of HZSM-5(225), HPWA and 20%HPWA/HZSM-5(225) composite catalyst.

Table 2.8 XRD data of HZSM-5(225), HPWA and 20%HPWA/HZSM-5(225) composite catalyst.

HZSM-5(225)		HPWA		20%HPWA/HZSM-5(225)	
d (Å)	I/I0	d (Å)	I/I0	d (Å)	I/I0
11.05	100	15.22	9	11.05	78
10.00	60	12.9	70	10.05	100
5.97	24	11.10	25	8.33	12
4.90	8	10.15	100	6.70	28
4.25	2	9.50	42	5.90	11
3.85	47	8.11	10	5.74	13
3.71	40	6.14	5	4.97	34
3.62	25	5.90	5	4.61	18
3.43	10	5.09	25	4.26	22
3.30	11	4.81	29	3.83	75
3.05	2	4.59	19	3.71	5
2.98	9	4.38	26	3.62	11
2.00	4	4.07	13	3.37	53
		3.53	19	2.97	16
		3.34	38	2.72	9
		3.27	20	2.47	12
		3.18	77	2.33	9
		3.06	30	2.00	10
		2.51	43	186	8
		2.33	44		
		2.00	13		
		1.86	11		

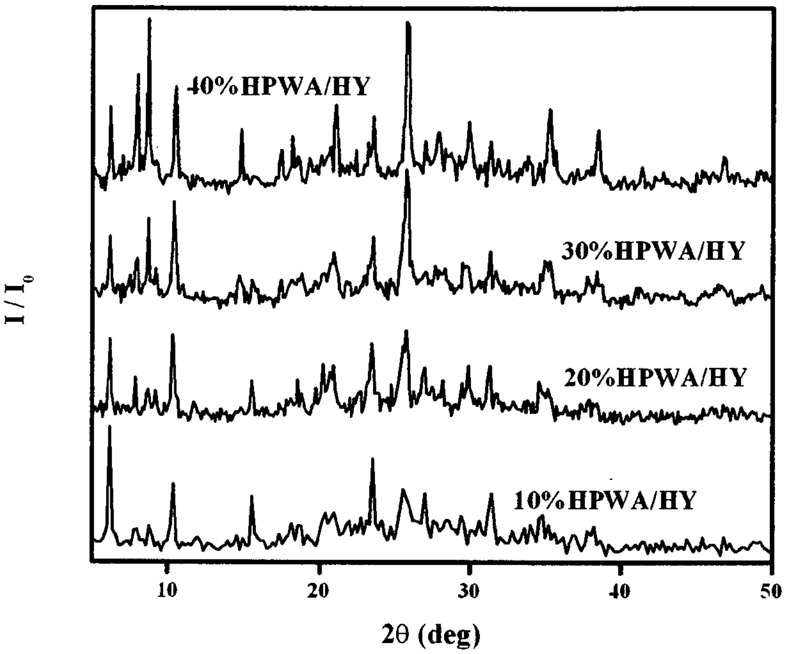

Figure 2.5 XRD profiles of of various HPWA/HY composite catalysts.

Table 2.9 XRD data of various HPWA/HY composite catalysts.

10%HPWA/HY		20%HPWA/HY		30%HPWA/HY		40%HPWA/HY	
d (Å)	I/I0	d (Å)	I/I0	d (Å)	I/I0	d (Å)	I/I0
14.24	100	14.24	96	14.24	53	14.24	51
12.54	28	12.54	25	12.54	10	12.54	23
11.93	30	11.93	24	11.93	10	11.93	20
11.04	23	11.04	29	11.04	37	11.04	69
10.15	28	10.15	43	10.15	65	10.15	100
9.81	29	9.81	18	9.81	10	9.81	6
8.72	60	8.72	100	8.72	77	8.72	62
7.54	32	7.54	28	7.54	10	7.54	11
5.96	6	5.96	10	5.96	25	5.96	38
5.69	51	5.69	51	5.69	18	5.69	10
5.06	16	5.06	22	5.06	22	5.06	27
4.87	29	4.87	31	4.87	22	4.87	34
4.57	28	4.57	52	4.57	30	4.57	20
4.40	25	4.40	69	4.40	20	4.40	24
4.21	26	4.21	53	4.21	42	4.21	52
4.07	20	4.07	28	4.07	19	4.07	18
3.92	24	3.92	39	3.92	29	3.92	27
3.76	77	3.76	92	3.76	40	3.76	46
3.47	54	3.47	82	3.47	100	3.47	98
3.29	51	3.29	66	3.29	28	3.29	21
3.19	31	3.19	44	3.19	29	3.19	37
3.11	58	3.11	53	3.11	30	3.11	25
2.99	34	2.99	68	2.99	37	2.99	42
2.85	51	2.85	38	2.85	31	2.85	32
2.54	36	2.54	47	2.54	43	2.54	50
2.34	27	2.34	29	2.34	29	2.34	34
2.18	15	2.18	19	2.18	10	2.18	18
1.94	11	1.94	25	1.94	19	1.94	23
1.84	14	1.84	15	1.84	19	1.84	10

The X ray diffractograms of ZSM-5 zeolites showed two major characteristic peaks at d = 11.05 Å and 3.85 Å. Also a high degree of crystallinity is reflected by the spectra. The X ray diffractogram of HY zeolite showed maximum intensity peak at d = 14.24 Å which is in accordance with reported literature [286]. Also a high degree of crystallinity is reflected by the spectra. The X ray diffractograms of β zeolites showed two major characteristic peaks at d = 11.20 Å and 3.92 Å which are similar to reported data for β zeolites by Newsman et. al. [287]. HPWA showed the maximum intensity peak at d = 10.05 Å. Figure 2.4 shows that the maximum intensity peak for the composite catalyst 20%HPWA/HZSM-5(225) is at d = 10.00 Å. A synergism is observed at this d value wherein the medium intensity peak of HZSM-5(225) combines with the maximum intensity peak of HPWA to give a resultant high absorption. This indicates an interaction between HPWA and HZSM-5(225) zeolite, which is reported to be more likely at lower weight % loading of HPWA on support as in this case [289]. An additional absorption peak which is not present in both the pure catalysts is observed at d = 3.37 Å which may have been due to this interaction. The X ray diffractograms of various composite catalysts of HPWA and HY shown in Figure 2.5 indicates a progressive growth in intensities of HPWA as HPWA content increases in the composite catalysts. It is in accordance with literature report that the Keggin structure of HPWA is reflected more at higher loading levels. Additional strong absorption peaks are observed at d = 8.72 Å and d = 3.47 Å in the composite catalysts of all compositions which are not present in both the pure catalysts. These peaks could be generated out of the interaction between the two highly acidic pure catalysts. Thus X ray studies reveal that HPWA interacts with zeolite supports in case of both HZSM-5(225) as well as HY zeolite. Additional acid sites may be generated due to this interaction between HPWA and the zeolites and also there can be modification of acid sites present in the pure catalysts. This may be interesting from the point of view of acidity of the catalysts as well as catalytic applications.

2.2.2. Infrared spectroscopy

The IR studies were carried out on a Shimadzu IRPrestige-21 FTIR in the range of 1300 – 400 cm^{-1}. Figure 2.6 to Figure 2.12 show the IR spectra of various catalysts and the corresponding IR band assignments are shown in Table 2.10 to Table 2.14.

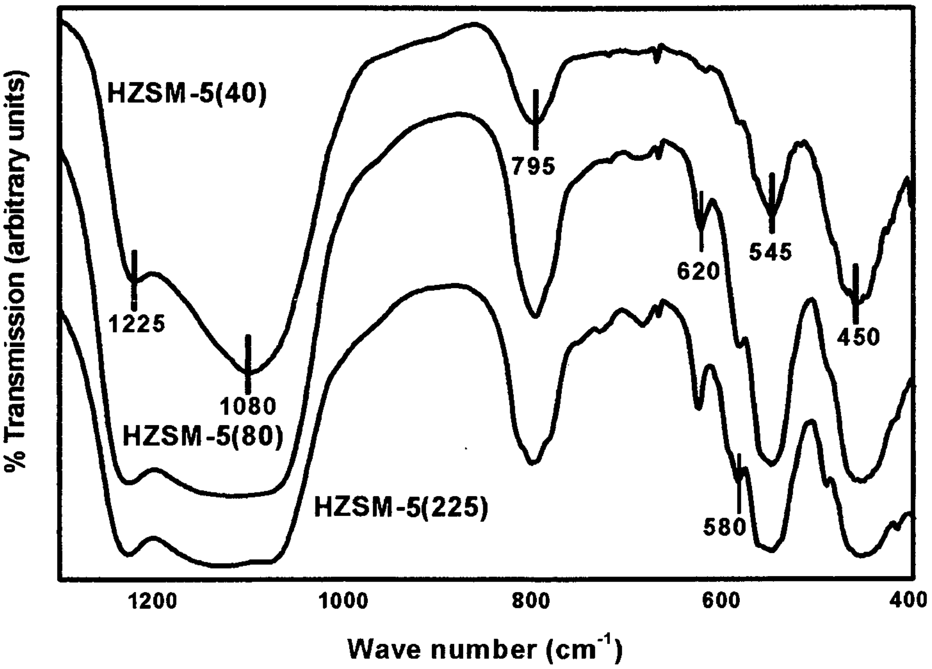

Figure 2.6 IR spectra of HZSM-5 zeolites of different Si/Al ratios.

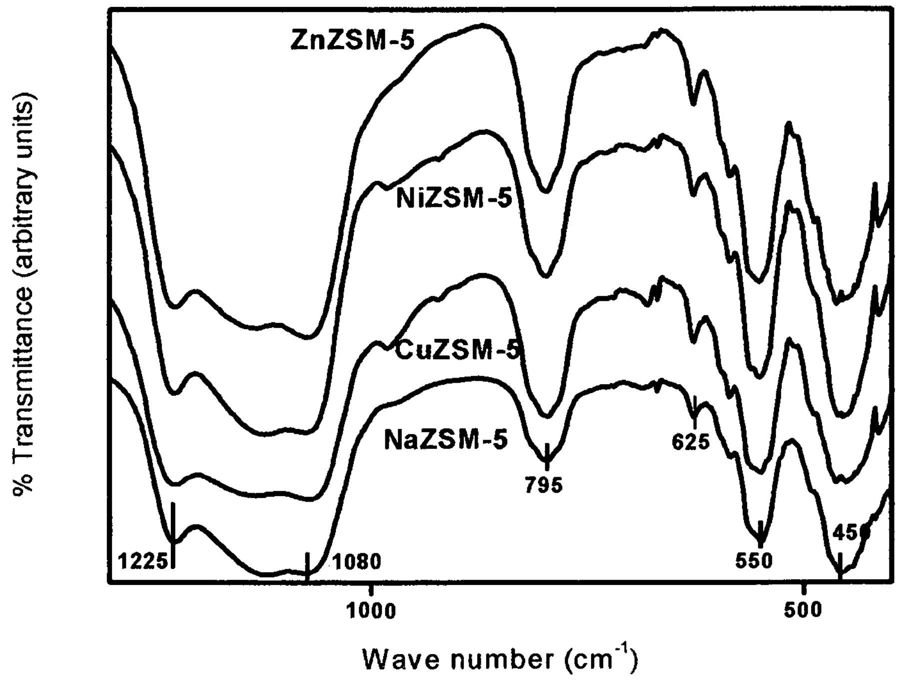

Figure 2.7 IR spectra of various ZSM-5 zeolites.

Table 2.10 IR band assignment of ZSM-5 zeolite frameworks.

Catalyst	Asymmetric stretching		Symmetric stretching		Double ring	T – O bending
	External	Internal	External	Internal		
ZSM-5 [227]	1220	1085	795 755		620 570 545	450
HZSM-5(40)	1220 (s)	1090 (s)	795 (m) 750 (w)		620 (w) ---- 545 (m)	450 (s)
HZSM-5(80)	1220 (m)	1090 (m)	795 (s)		620 (w) 580 (w) 545 (m)	450 (s)
HZSM-5(225)	1220 (m)	1090 (m)	795 (s)		620 (w) 580 (w) 545 (s)	450 (m)
NaZSM-5	1225 (m)	1080 (m)	795 (s)		625 (w) 580 (w) 550 (s)	450 (s)
CuZSM-5	1225 (m)	1080 (m)	795 (s)		625 (w) 580 (w) 550 (s)	450 (s)
NiZSM-5	1225 (m)	1080 (m)	795 (s)		625 (w) 580 (w) 550 (s)	450 (s)
ZnZSM-5	1225 (m)	1080 (m)	795 (s)		625 (w) 580 (w) 550 (s)	450 (s)

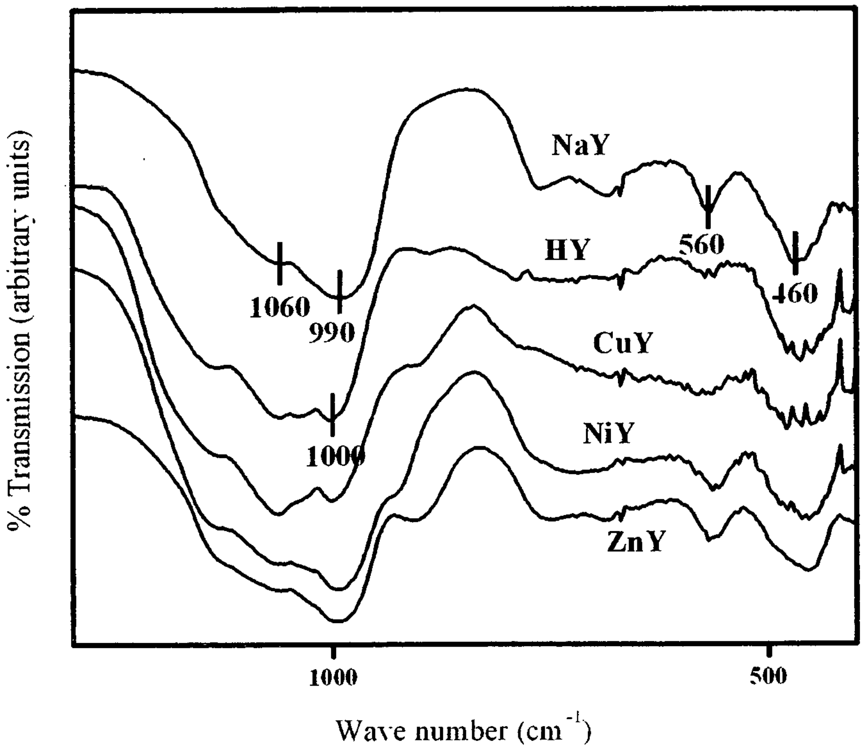

Figure 2.8 IR spectra of various Y zeolites.

Table 2.11 IR band assignment of Y zeolite frameworks.

Catalyst	Asymmetric stretching		Symmetric stretching		Double ring	T – O bending
	External	Internal	External	Internal		
NaY [288]	1130	1005	784	714	572	455
NaY	1060 (m)	990 (s)	760 (w)	680 (w)	560 (m)	460 (s)
HY	1060 (m)	1000 (s)	760 (w)	680 (w)	560 (m)	460 (s)
CuY	1060 (m)	990 (s)	760 (w)	680 (w)	560 (m)	460 (s)
NiY	1060 (m)	990 (s)	760 (w)	680 (w)	560 (m)	460 (s)
ZnY	1060 (m)	990 (s)	760 (w)	680 (w)	570 (m)	460 (s)

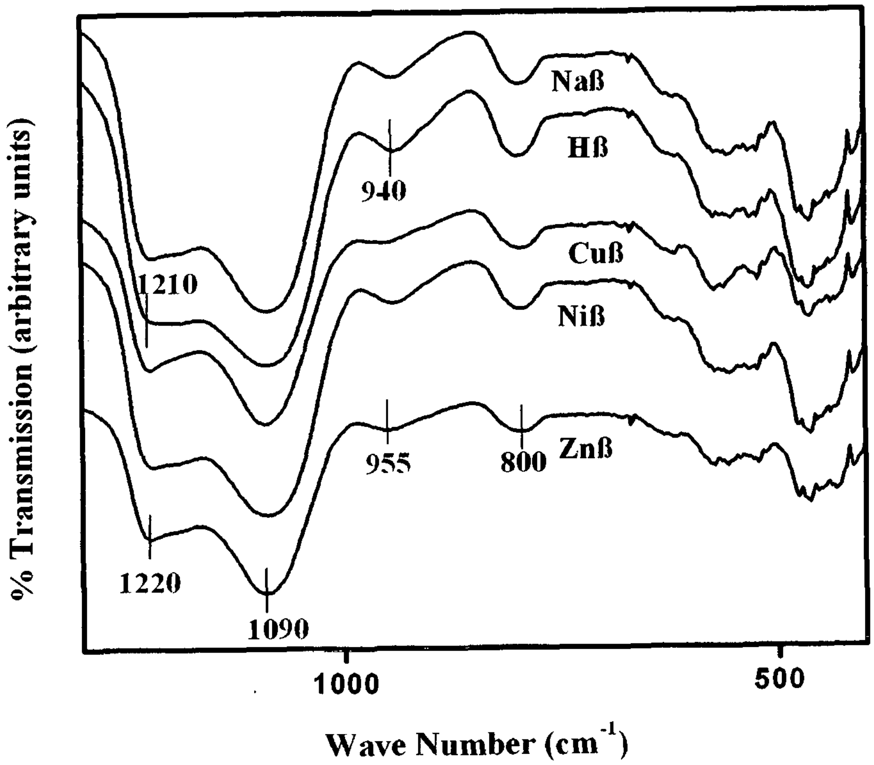

Figure 2.9 IR spectra of various β zeolites.

Table 2.12 IR band assignment of β zeolite frameworks.

Catalyst	Asymmetric stretching		Symmetric stretching		Double ring	T – O bending
	External	Internal	External	Internal		
Beta [227]	1220	1080	850		575	475
		930	800		525	430
Naβ	1220 (m)	1090 (s)	--		560 (w)	465(w)
		955 (w)	800 (m)		525 (w)	435 (w)
Hβ	1210 (m)	1090 (s)	--		550 (w)	465(w)
		940 (w)	800 (s)		525 (w)	440 (w)
Cuβ	1220 (m)	1090 (s)	--		560 (w)	465(w)
		955 (w)	800 (s)		525 (w)	435 (w)
Niβ	1220 (m)	1090 (s)	--		560 (w)	465(w)
		955 (w)	800 (s)		525 (w)	435 (w)
Znβ	1220 (m)	1090 (s)	--		560 (w)	465(w)
		955 (w)	800 (m)		525 (w)	435 (w)

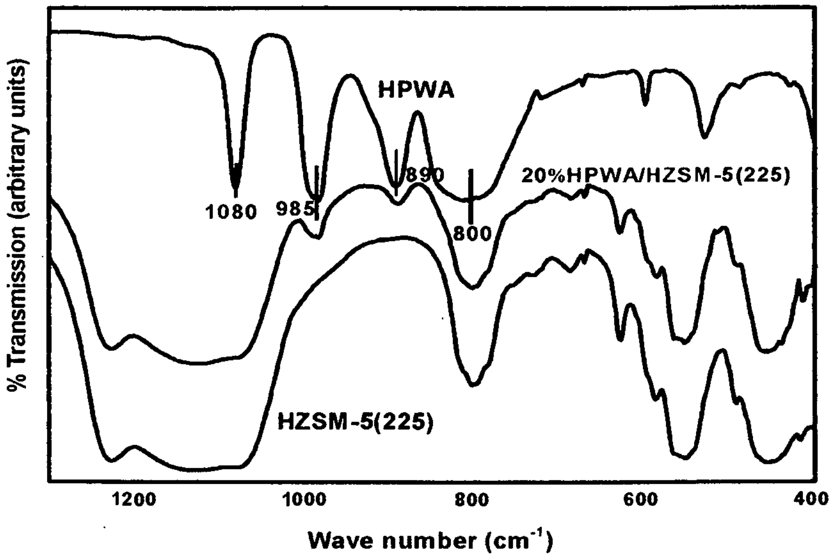

Figure 2.10 IR spectra of HPWA, HZSM-5(225) and 20%HPWA/HZSM-5(225) composite catalyst.

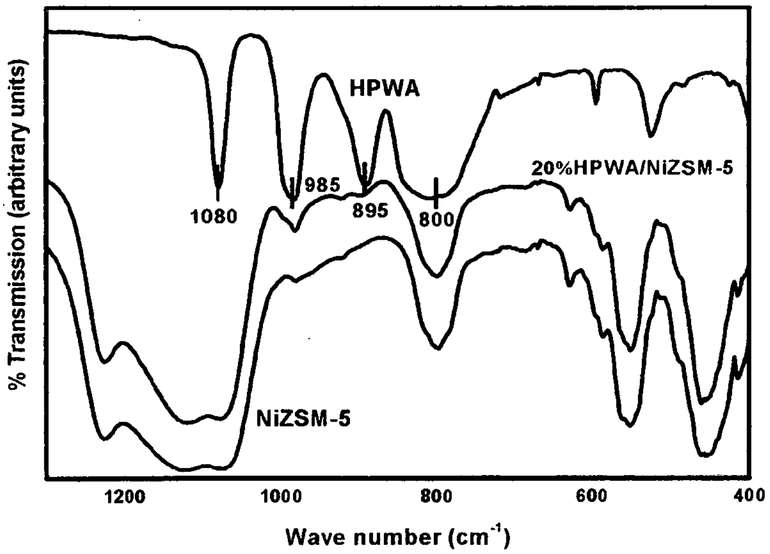

Figure 2.11 IR spectra of HPWA, NiZSM-5 and 20%HPWA/NiZSM-5 composite catalyst.

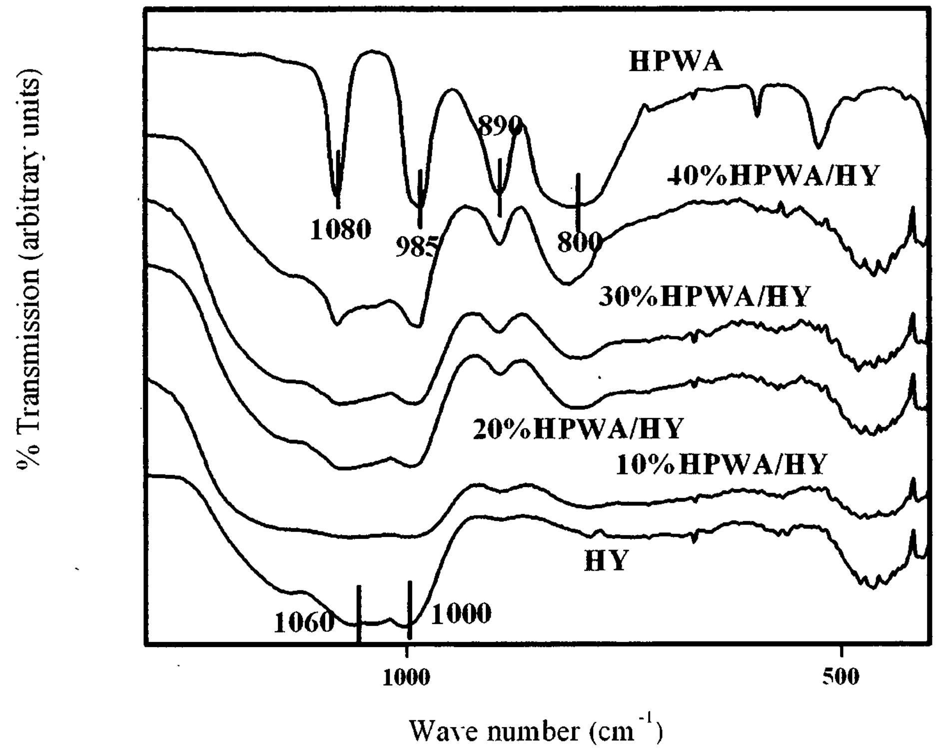

Figure 2.12 IR spectra of HPWA, HY and various HPWA/HY composite catalysts.

The frequency values observed for ZSM-5 zeolites were in agreement with the reported literature [227]. No significant change was observed upon ion exchange. The Y zeolite frequencies showed a slight variation of frequencies from a reported literature, which could be due to the differences in Si/Al ratios between the reported and the Y zeolite used in this investigation. However there was not much significant change upon ion exchange with NaY zeolite. All the β zeolite catalysts exhibited similar IR spectra.

IR band assignments of HPWA were in accordance with the literature values as can be seen from Table 2.13.

Table 2.13 IR band assignments of HPWA.

HPWA	P-O bond	Terminal W-O	Corner shared bridge bond W-O-W	Edge shared bridge bond W-O-W
Literature	1082	984	892	800
Present work	1080 (s)	985 (s)	890 (s)	800 (s),

A comparison of IR spectra of HZSM-5(225), HPWA and 20%HPWA/HZSM-5(225) from Figure 2.10 shows that the Keggin structure frequencies of HPWA show significant absorption in the composite catalyst. However in the case of 20%HPWA/NiZSM-5, it is observed that the 890 cm^{-1} band corresponding to corner shared bridge bond W-O-W does not show any absorption in the composite catalysts as can be seen from Figure 2.11. It is observed from Figure 2.12 that as the concentration of HPWA increases from 10 % to 40 % in the composite catalysts of HPWA and HY, the Keggin structure bands of HPWA grow in intensity. Thus at higher loadings of HPWA on the support the bulk properties of HPAs prevail as reported in literature.

2.2.3 BET surface area measurements

The BET surface areas of various catalysts were determined using a Smartsorb 91 surface area analyser. The BET surface area of the various catalysts is shown in Table 2.14.

Table 2.14 BET surface area of carious catalysts.

Catalyst	BET surface area (m^2/g)
HZSM-5(40)	358
HZSM-5(80)	325
HZSM-5(225)	305
NaZSM-5 (Si/Al =40)	294
CuZSM-5	296
NiZSM-5	286
ZnZSM-5	289
NaY	475
HY	515
CuY	503
NiY	475
ZnY	495
Naβ	460
Hβ	472
Cuβ	457
Niβ	468
Znβ	464
Phosphotungstic acid (HPWA)	11
20%HPWA/HZSM-5(225)	212
20%HPWA/NiZSM-5	205
10%HPWA/HY	405
20%HPWA/HY	378
30%HPWA/HY	346
40%HPWA/HY	292
NiZSM-5(225) (Si/Al =225)	294

The BET surface areas of various ZSM-5 zeolites were observed to be nearly equal. The Y and β zeolites exhibited a much higher BET surface area as compared to ZSM-5 zeolites. HY exhibited the highest BET surface area among the various catalysts used in this investigation. HPWA exhibited a low BET surface area (11 m^2 / g) as reported in the literature [289]. However the composite catalysts showed significantly higher BET surface area. This emphasises the importance of dispersing HPAs on high surface area supports for catalytic applications. For the HPWA/HY composite catalysts of different compositions, the BET surface area decreased progressively with an increase in HPWA content.

2.2.4 Acidity Measurements

Acidity of all the catalysts was measured using temperature programmed desorption (TPD) technique with ammonia as a probe molecule. 100 mg of a catalyst sample was packed in a catalytic reactor (as shown in Figure 2.13) and activated in air at 500 ^{o}C for about 6 hours. The catalyst was then cooled to room temperature in flowing dry 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 ^{o}C per minute and the amount of ammonia desorbed as a function of temperature was calculated using titrimetry. The acidity values, TPD profiles and the total acidity values of the catalysts are presented below.

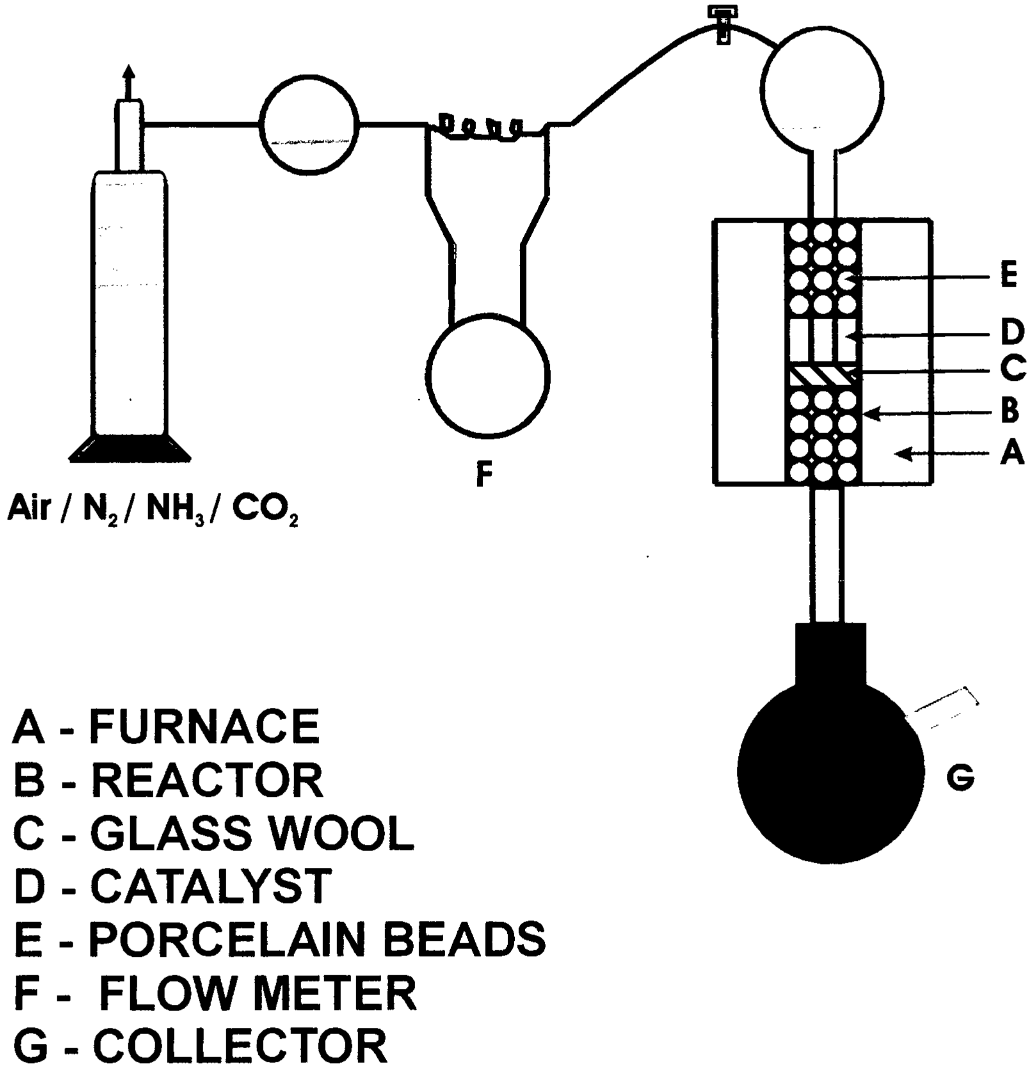

Fig. 2.13 Set up for TPD studies.

Table 2.15 Acidity data of various ZSM-5 zeolite catalysts.

Temperature range (°C)	Acidity (mmol / g)						
	HZSM-(40)	HZSM-(80)	HZSM-5(225)	NaZSM-5	CuZSM-5	NiZSM-5	ZnZSM-5
40-80	0.08593	0.06451	0.00782	0.01082	0.01742	0.01932	0.01082
80-120	0.08627	0.04496	0.01058	0.00907	0.01802	0.02875	0.02621
120-160	0.06942	0.03077	0.00612	0.00308	0.00943	0.01932	0.00182
160-200	0.05210	0.01092	0.00374	0.00308	0.00832	0.02875	0.00932
200-240	0.08791	0.03077	0.00489	0.00212	0.01703	0.00908	0.00673
240-280	0.02082	0.02084	0.00447	0.00212	0.00943	0.00853	0.00527
280-320	0.02074	0.01092	0.00698	0.00072	0.00133	0.00613	0.00391
320-360	0.02574	0.00783	0.00812	0.00212	0.00687	0.00195	0.00168
360-400	0.00952	0.00783	0.00673	0.00108	0.00691	0.00582	0.00128
400-440	0.00831	0.00324	0.00684	0.00162	0.00153	0.00161	0.00096
440-480	0.00695	0.00187	0.00335	0.00091	0.00128	0.00098	0.00124

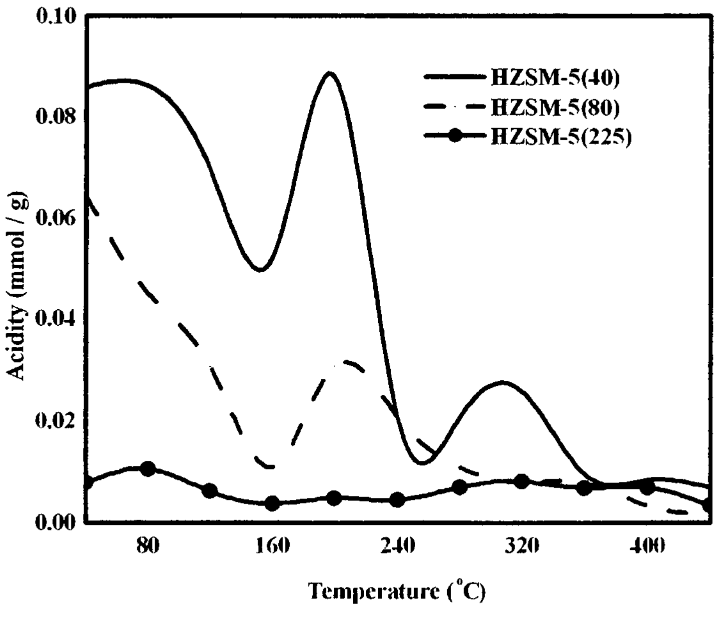

Figure 2.14 Acidity profiles of HZSM-5(40), HZSM-5(80) and HZSM-5(225) zeolite.

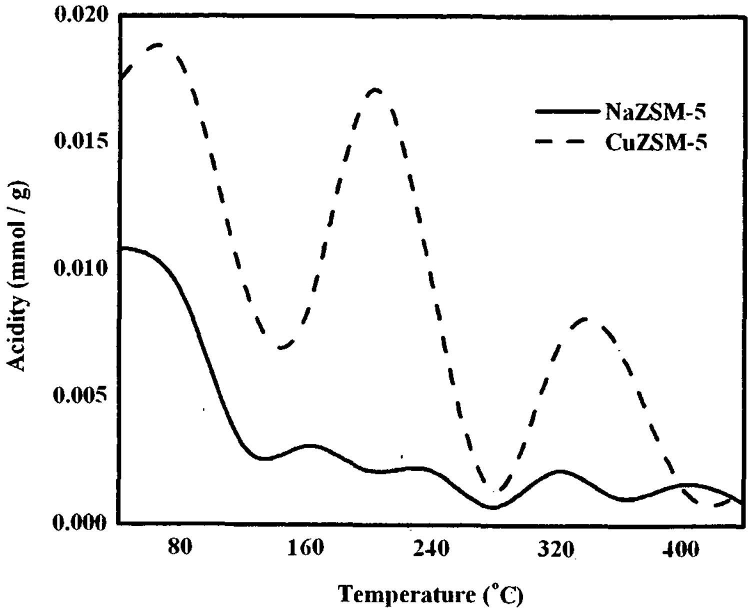

Figure 2.15 Acidity profiles of NaZSM-5 and CuZSM-5 zeolite.

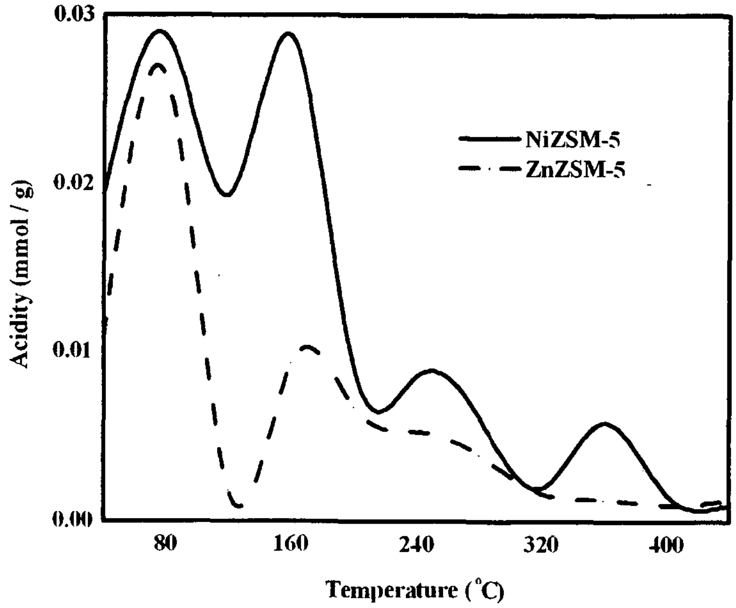

Figure 2.16 Acidity profiles of NiZSM-5 and ZnZSM-5 zeolite.

Table 2.16 Acidity data of various Y zeolite catalysts.

Temperature range (°C)	Acidity (mmol / g)				
	NaY	HY	CuY	NiY	ZnY
40-80	0.00456	0.01348	0.01806	0.02216	0.01753
80-120	0.06104	0.02503	0.05117	0.07432	0.04923
120-160	0.01904	0.02952	0.05884	0.06139	0.01740
160-200	0.00153	0.05148	0.02263	0.02194	0.00921
200-240	0.00264	0.06342	0.02578	0.00198	0.00194
240-280	0.00387	0.04785	0.01229	0.00761	0.00317
280-320	0.00126	0.02598	0.01171	0.00308	0.00242
320-360	0.00139	0.04371	0.00285	0.00169	0.00186
360-400	0.00104	0.03815	0.00572	0.00108	0.00751
400-440	0.00103	0.02178	0.00178	0.00149	0.00257
440-480	0.00097	0.02485	0.00207	0.00093	0.00194

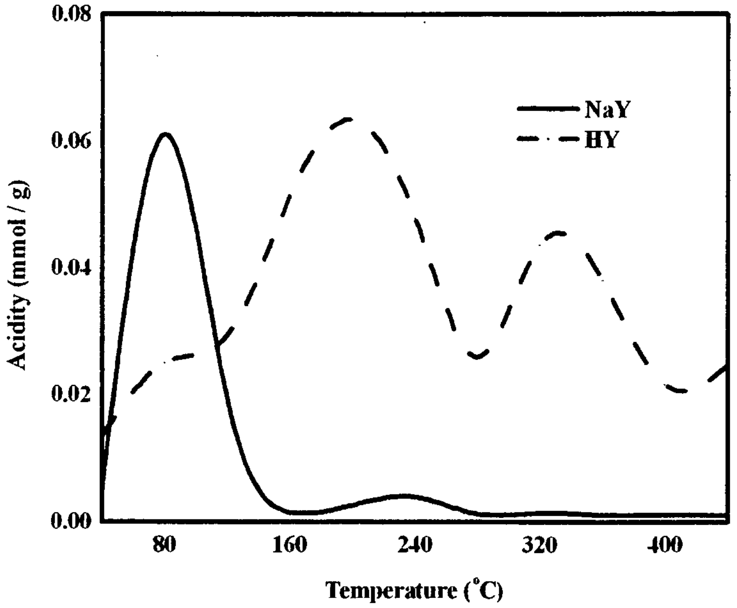

Figure 2.17 Acidity profiles of NaY and HY zeolite.

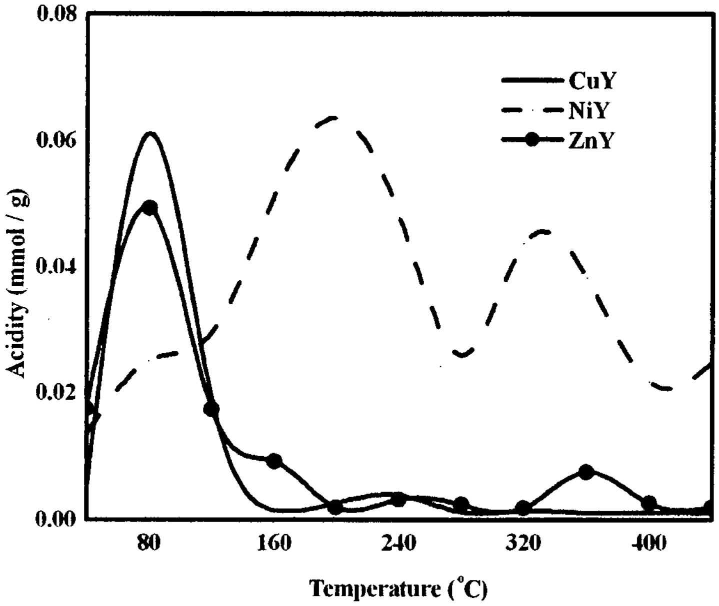

Figure 2.18 Acidity profiles of CuY, NiY and ZnY zeolite.

Table 2.17 Acidity data of various β zeolite catalysts.

Temperature range (°C)	Acidity (mmol / g)				
	Naβ	Hβ	Cuβ	Niβ	Znβ
40-80	0.01407	0.03928	0.02738	0.02254	0.00954
80-120	0.02137	0.04793	0.02922	0.01813	0.01319
120-160	0.01065	0.06952	0.01856	0.00682	0.06318
160-200	0.01514	0.07539	0.01921	0.00448	0.01592
200-240	0.01248	0.06892	0.02713	0.00538	0.03576
240-280	0.01298	0.06124	0.01248	0.01735	0.01934
280-320	0.00812	0.00935	0.00439	0.01289	0.00735
320-360	0.00874	0.01893	0.00962	0.03864	0.00921
360-400	0.01293	0.03528	0.01462	0.02108	0.00215
400-440	0.00914	0.04926	0.00941	0.01169	0.00818
440-480	0.00825	0.01184	0.00638	0.00753	0.01093

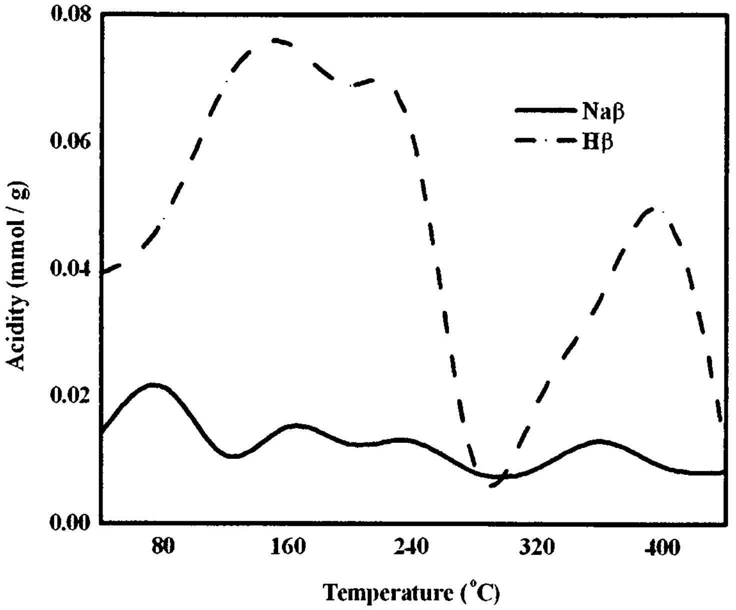

Figure 2.19 Acidity profiles of Naβ and Hβ zeolite.

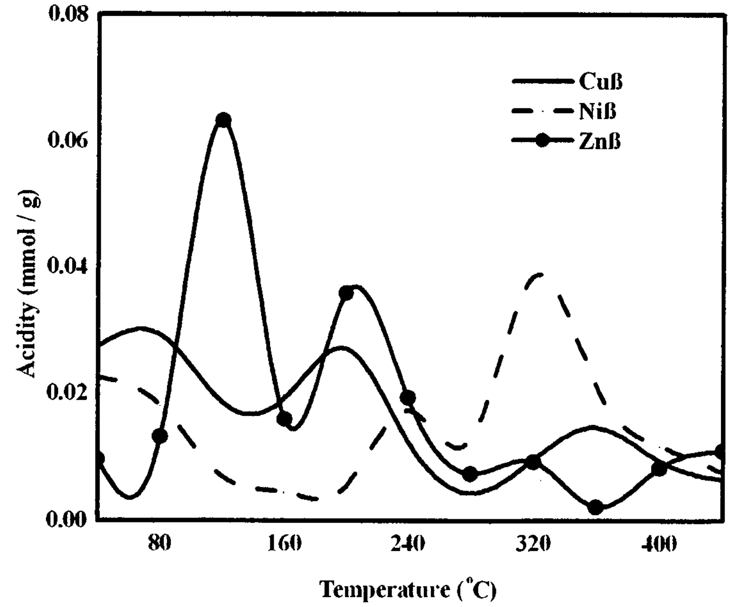

Figure 2.20 Acidity profiles of Cuβ, Niβ and Znβ zeolite.

Table 2.18 Acidity data of HPWA and HPWA modified with ZSM-5 zeolite.

Temperature range (°C)	Acidity (mmol / g)		
	HPWA	20%HPWA/HZSM-(225)	20%HPWA/NiZSM-5
40-80	0.04682	0.01458	0.02583
80-120	0.06132	0.02007	0.01792
120-160	0.08456	0.02163	0.01835
160-200	0.05402	0.01236	0.01014
200-240	0.04758	0.01648	0.01382
240-280	0.05126	0.01895	0.01253
280-320	0.04934	0.02034	0.01782
320-360	0.05908	0.02142	0.04386
360-400	0.02812	0.02173	0.02953
400-440	0.01063	0.02484	0.02473
440-480	0.00842	0.02127	0.00981

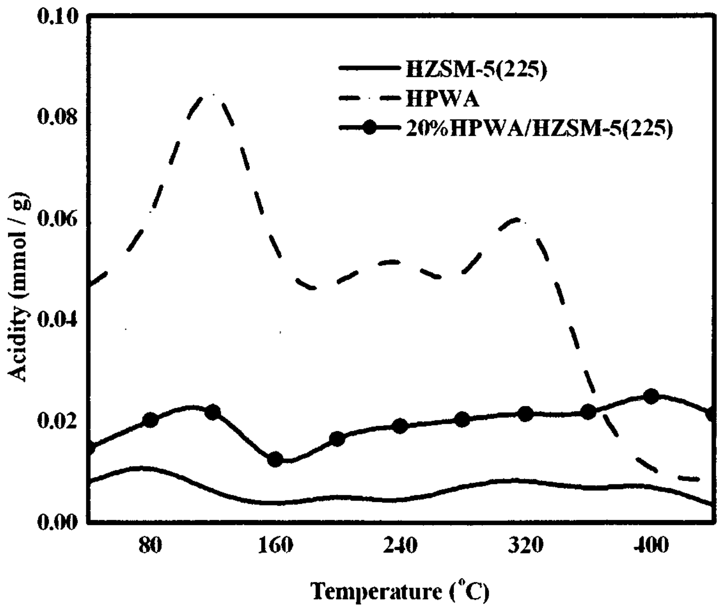

Figure 2.21 Acidity profiles of HZSM-5(225), HPWA and 20%HPWA/HZSM-5 (225) composite catalyst.

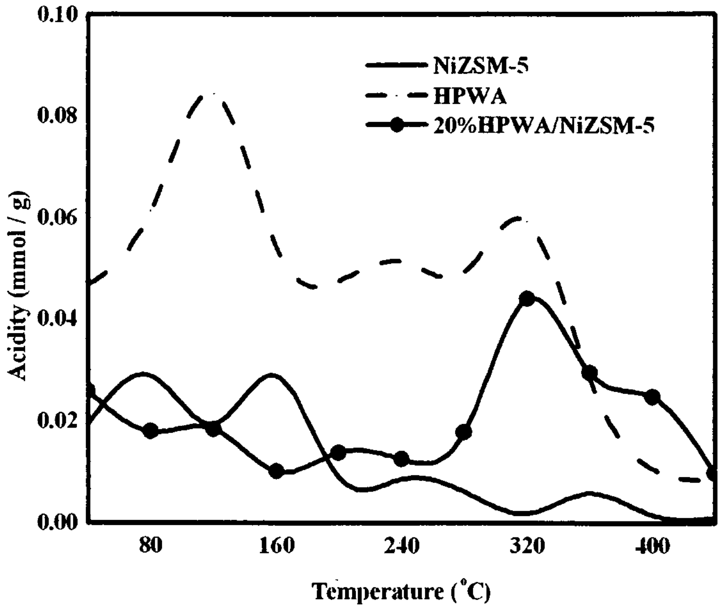

Figure 2.22 Acidity profiles of NiZSM-5, HPWA and 20%HPWA/NiZSM-5 composite catalyst.

Table 2.19 Acidity data of HPWA and HPWA/HY composite catalysts of different compositions.

Temperature range (°C)	Acidity (mmol / g)				
	HPWA	10%HPWA/HY	20%HPWA/HY	30%HPWA/HY	40%HPWA/HY
40-80	0.0468	0.02452	0.04154	0.03583	0.04218
80-120	0.0613	0.04983	0.03654	0.05143	0.02597
120-160	0.0845	0.03735	0.04998	0.02785	0.03284
160-200	0.0540	0.04056	0.02076	0.02452	0.04716
200-240	0.0475	0.02958	0.03282	0.02801	0.05912
240-280	0.0512	0.04082	0.01154	0.03894	0.07138
280-320	0.0493	0.02548	0.03388	0.01783	0.04219
320-360	0.0590	0.02313	0.03202	0.04285	0.03136
360-400	0.0281	0.01753	0.03107	0.05394	0.03849
400-440	0.0106	0.02047	0.03501	0.03871	0.02741
440-480	0.0084	0.01652	0.03012	0.03422	0.01512

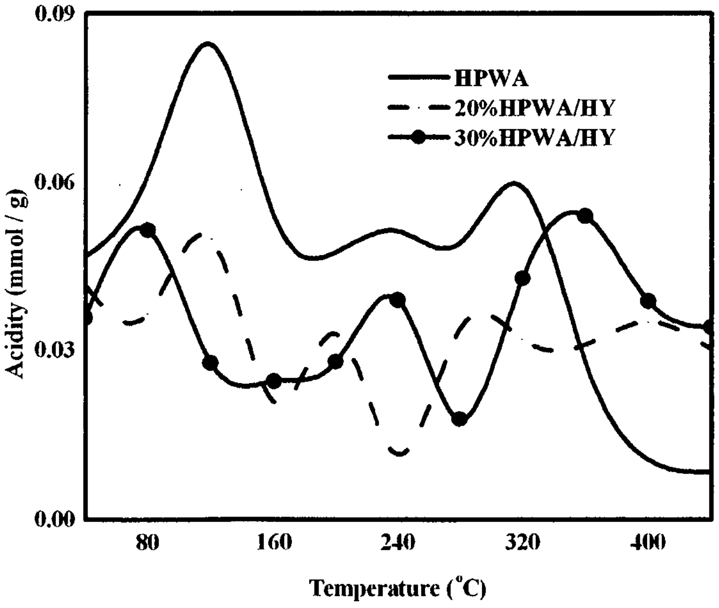

Figure 2.23 Acidity profiles of HPWA and HPWA/HY composite catalysts (Profiles of two representative compositions are shown).

Table 2.20 Total acidity data of various catalysts.

Catalyst	Total acidity (mmol / g)
HZSM-5(40)	0.47371
HZSM-5(80)	0.23446
HZSM-5(225)	0.06964
NaZSM-5	0.03674
CuZSM-5	0.09757
NiZSM-5	0.13024
ZnZSM-5	0.06924
NaY	0.09837
HY	0.38525
CuY	0.21290
NiY	0.19767
ZnY	0.11478
Naβ	0.13387
Hβ	0.48694
Cuβ	0.17840
Niβ	0.16653
Znβ	0.19475
HPWA	0.50115
20%HPWA/HZSM-5(225)	0.21367
20%HPWA/NiZSM-5	0.22434
10%HPWA/HY	0.32579
20%HPWA/HY	0.35528
30%HPWA/HY	0.39413
40%HPWA/HY	0.43322

HZSM-5 (40) zeolite was found to be the most acidic zeolite among the various ZSM-5 zeolites studied in this work. For the three HSM-5 zeolites of different Si/Al ratios the total acidity decreased with an increase in Si/Al ratio. NaZSM-5 zeolite was found to exhibit the lowest total acidity among the ZSM-5 zeolites. Metal ion exchange of transition metal ions with NaZSM-5 resulted in an increase in acidity.

The protonic zeolite, i. e. HY zeolite was found to be the most acidic catalyst among the various Y zeolite catalysts studied. The sodium form i. e. NaY zeolite was found to possess the lowest total acidity among the various Y zeolite catalysts. The total acidity followed the order NaY < ZnY < NiY < CuY < HY.

The protonic zeolite, i. e. Hβ zeolite was found to be the most acidic catalyst among the various β zeolite catalysts studied and possessed the highest total acidity from all the zeolite catalysts used in this investigation. The sodium form i. e. Naβ zeolite was found to be the least acidic catalyst among the various β zeolite catalysts. The total acidity followed the order Naβ < Niβ < Cuβ < Znβ < Hβ.

HPWA exhibited a high total acidity (Total acidity = 0.50115 mmol / g). HPWA was found to be more acidic than zeolites. HPWA is previously reported to possess a higher acidity compared to zeolites [252 - 254]. A Hammett indicators test has suggested $H_3PW_{12}O_{40}$ to be a superacid [253 - 256]. Calorimetric titrations carried out in acetonitrile have indicated that anhydrous $H_3PW_{12}O_{40}$ is a superacid [258].

The composite catalysts of HPWA with ZSM-5 zeolites i. e. 20%HPWA/HZSM-5(225) and 20%HPWA/NiZSM-5 showed a lower total acidity compared to HPWA. Such a change of acid strength of HPAs on supports is previously reported [264]. Both the catalysts exhibited an intermediate total acidity than the individual catalysts. Apart from this modification of acid sites at different temperatures when compared with acidity profiles of individual catalysts was also observed.

The composite catalysts of HPWA with HY zeolite showed variable acid strengths. Interestingly two composite catalysts 10%HPWA/HY and 20%HPWA/HY showed a lower total acidity than both the individual catalysts, whereas the other two composite catalysts viz. 30%HPWA/HY and 40%HPWA/HY exhibited intermediate total acidity values compared to that of pure catalysts. The reason for this could be the interaction of HPWA with the support. HPAs are known to interact strongly with supports at low loading levels. The bulk properties of HPAs prevail more at high loading levels. The modification of acid sites in the composite catalysts can be attributed to the interaction that may take place between the two acidic catalysts. XRD studies have revealed the generation of additional peaks, which are not observed in either of the pure catalysts, generated in the composite catalysts exhibiting strong absorption. Owing to this interaction between HPWA and the zeolites additional acid sites may be generated or there may be modification of acid sites present in the pure catalysts.

2.2.5 Basicity Measurements

Basicity of zeolite and oxide samples is measured using temperature programmed desorption (TPD) technique with carbon dioxide as a probe molecule. 100 mg of a catalyst sample was packed in a catalytic reactor (set up is similar as shown in Figure 2.13) and activated in air at 500 °C for about 6 hours. The catalyst was then cooled to room temperature in flowing nitrogen. Carbon dioxide 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 carbon dioxide desorbed as a function of temperature was calculated. The basicity values, TPD profiles and the total basicity values of the catalysts are presented below.

Table 2.21 Basicity data of various ZSM-5 zeolite catalysts.

Temperature range (°C)	Basicity(μmol / g)						
	HZSM-5(40)	HZSM-5(80)	HZSM-5(225)	NaZSM-5	CuZSM-5	NiZSM-5	ZnZSM-5
40-80	0.00613	0.00198	0.00465	0.01073	0.00082	0.00053	0.00192
80-120	0.00445	0.01075	0.01017	0.00951	0.00079	0.00019	0.00208
120-160	0.00091	0.00741	0.00294	0.00682	0.00192	0.00209	0.00841
160-200	0.00064	0.00082	0.00218	0.01073	0.00462	0.00742	0.00386
200-240	0.00038	0.00082	0.00674	0.00812	0.00228	0.00412	0.00172
240-280	0.00143	0.00194	0.00218	0.00594	0.00109	0.00082	0.00289
280-320	0.00058	0.00285	0.00395	0.00386	0.00074	0.00097	0.00172
320-360	0.00028	0.00082	0.00295	0.00496	0.00085	0.00184	0.00094
360-400	0.00026	0.00064	0.00148	0.00328	0.00194	0.00263	0.00063
400-440	0.00024	0.00029	0.00218	0.00272	0.00069	0.00121	0.00038
440-480	0.00017	0.00018	0.00247	0.00175	0.00088	0.00192	0.00027

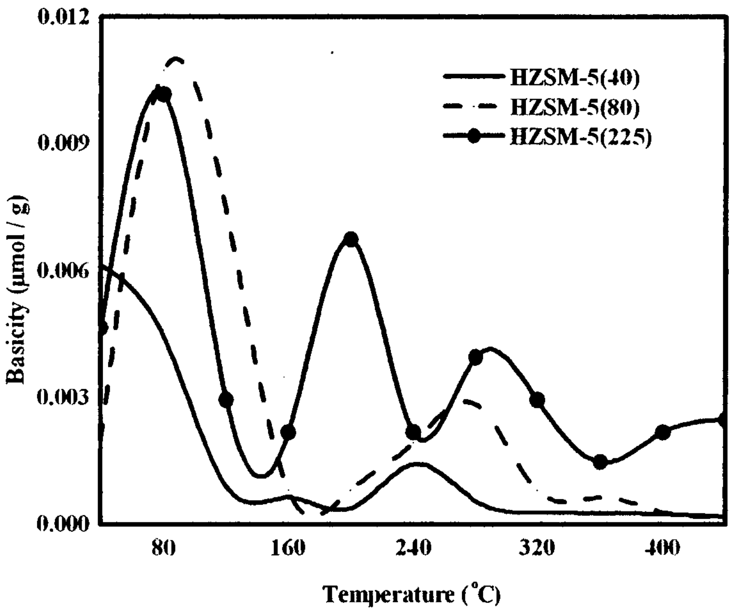

Figure 2.24 Basicity profiles of HZSM-5(40), HZSM-5(80) and HZSM-5(225) zeolite.

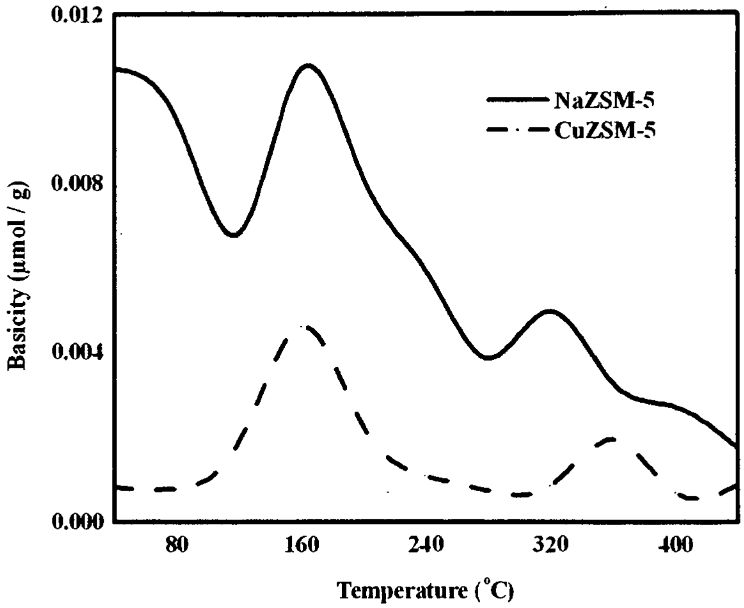

Figure 2.25 Basicity profiles of NaZSM-5 and CuZSM-5 zeolite.

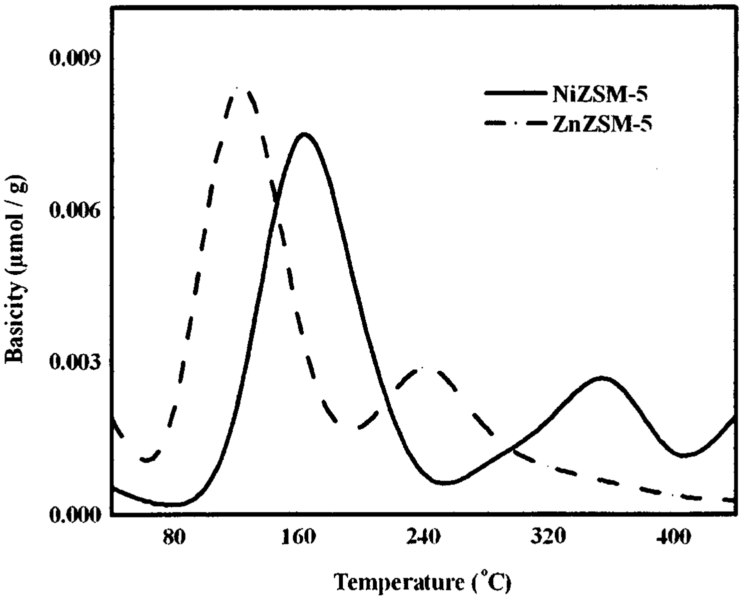

Figure 2.26 Basicity profiles of NiZSM-5 and ZnZSM-5 zeolite.

Table 2.22 Basicity data of various Y zeolite catalysts.

Temperature range (^{o}C)	Basicity(μmol / g)				
	NaY	HY	CuY	NiY	ZnY
40-80	0.00752	0.00591	0.00172	0.00195	0.00447
80-120	0.00642	0.00095	0.00413	0.00086	0.00692
120-160	0.00413	0.00307	0.00089	0.00712	0.00782
160-200	0.01074	0.00126	0.00107	0.00493	0.00341
200-240	0.01082	0.00126	0.00094	0.01024	0.00468
240-280	0.00752	0.00072	0.00182	0.00498	0.00293
280-320	0.00613	0.00048	0.00904	0.00271	0.00167
320-360	0.00523	0.00042	0.00691	0.00096	0.00292
360-400	0.00752	0.00078	0.00267	0.00084	0.00247
400-440	0.00168	0.00034	0.00083	0.00048	0.00248
440-480	0.00093	0.00026	0.00032	0.00075	0.00224

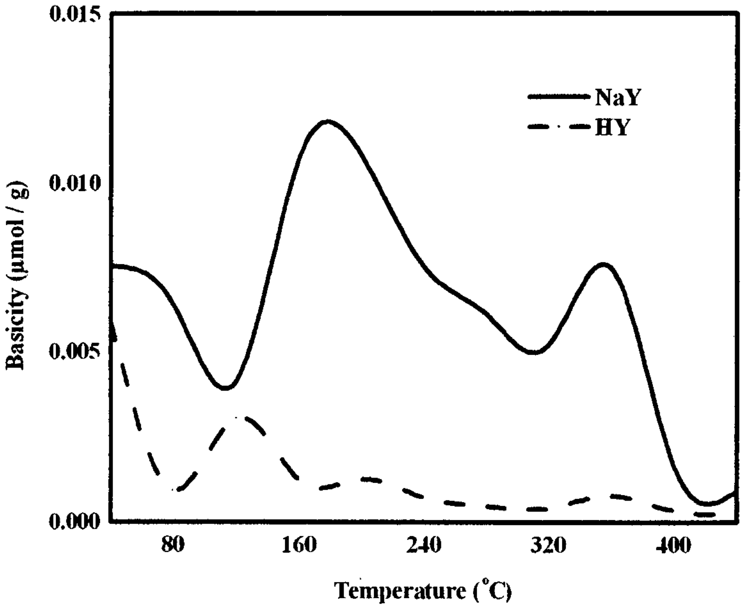

Figure 2.27 Basicity profiles of NaY and HY zeolite.

Figure 2.27 Basicity Profiles of NaY and HY Zeolite.

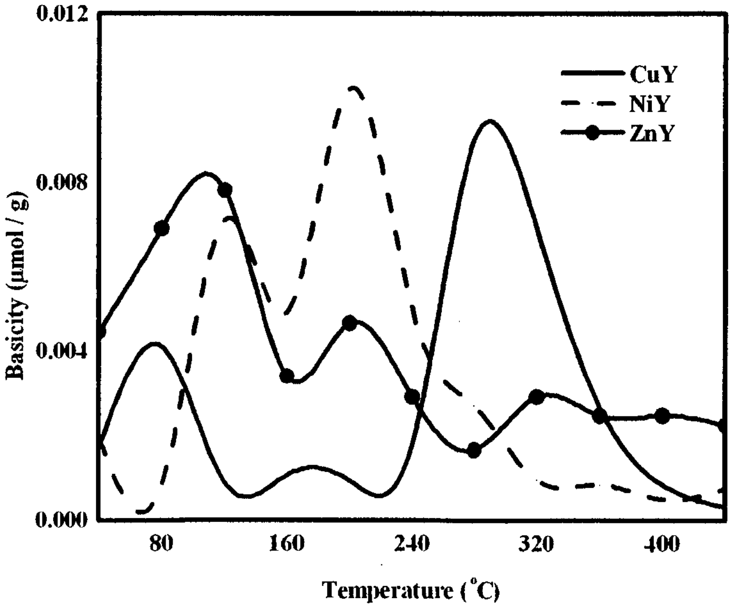

Figure 2.28 Basicity profiles of CuY, NiY and ZnY zeolite.

Figure 2.28 Basicity profiles of CuY, NiY and ZnY zeolite.

Table 2.23 Basicity data of various β zeolite catalysts.

Temperature range (°C)	Basicity(μmol / g)				
	Naβ	Hβ	Cuβ	Niβ	Znβ
40-80	0.01073	0.00731	0.00382	0.00842	0.00732
80-120	0.00468	0.00192	0.00292	0.00732	0.00254
120-160	0.01054	0.00174	0.00246	0.00458	0.00462
160-200	0.00730	0.00093	0.00232	0.00413	0.00258
200-240	0.00621	0.00093	0.00651	0.00357	0.00537
240-280	0.00419	0.00174	0.00228	0.00228	0.00438
280-320	0.00210	0.00042	0.00275	0.00246	0.00159
320-360	0.00107	0.00039	0.00462	0.00187	0.00089
360-400	0.00289	0.00034	0.00283	0.00194	0.00074
400-440	0.00129	0.00034	0.00231	0.00138	0.00217
440-480	0.00118	0.00028	0.00282	0.00092	0.00097

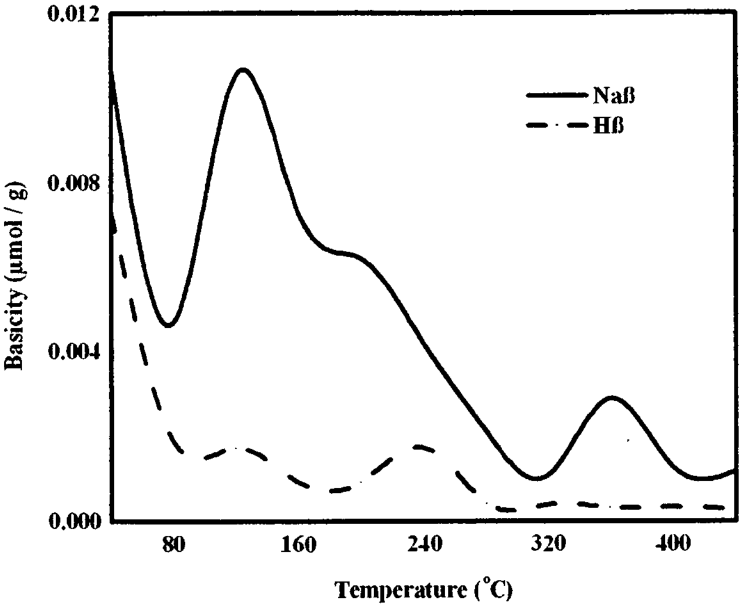

Figure 2.29 Basicity profiles of Naβ and Hβ zeolite.

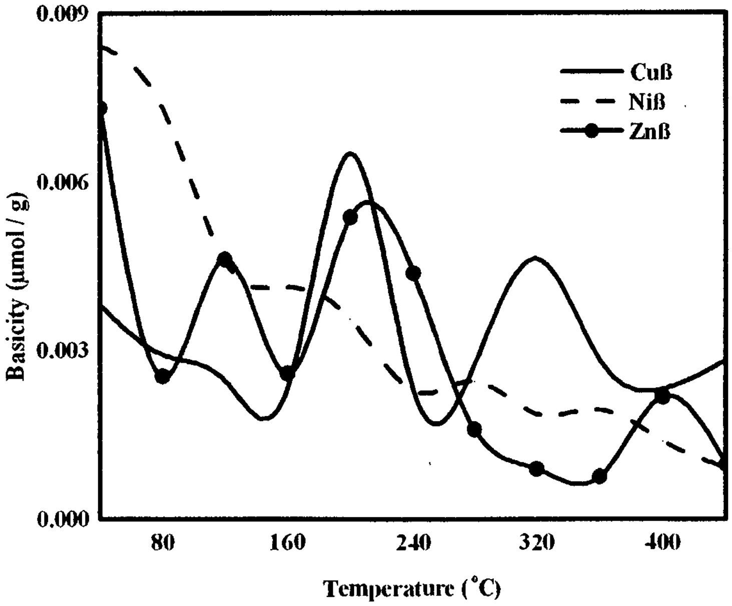

Figure 2.30 Basicity profiles of Cuβ, Niβ and Znβ zeolite.

Table 2.24 Total Basicity data of various zeolite catalysts.

Catalyst	Total basicity (μmol / g)
HZSM-5(40)	0.01547
HZSM-5(80)	0.02850
HZSM-5(225)	0.04189
NaZSM-5	0.06842
CuZSM-5	0.01662
NiZSM-5	0.02374
ZnZSM-5	0.02482
NaY	0.06864
HY	0.01545
CuY	0.03034
NiY	0.03582
ZnY	0.04201
Naβ	0.05218
Hβ	0.01634
Cuβ	0.03564
Niβ	0.03887
Znβ	0.03317

NaZSM-5 was found to possess the highest total basicity among the various ZSM-5 zeolites studied in this investigation. For the three HZSM-5 zeolites of different Si/Al ratios the total basicity followed the order HZSM-5(40) < HZSM-5(80) < HZSM-5(225). Thus an increase in Si/Al ratio of the zeolite seemed to increase the basicity of the HZSM-5 zeolites.

NaY zeolite was found to be the most basic catalyst among the various Y zeolite catalysts studied and possessed the highest total basicity from all the zeolite catalysts used in this investigation. The protonic form i. e. HY zeolite was found to possess the lowest total basicity among the various Y zeolite catalysts. The total basicity followed the order HY < NiY < CuY < ZnY < NaY. Interestingly, the total basicity followed a reverse order of that of total acidity.

The sodium form, i. e. Naβ zeolite was found to be the most basic catalyst among the various β zeolite catalysts studied. Hβ zeolite was found to possess the lowest total basicity among the various β zeolite catalysts. The total acidity followed the order Hβ < Cuβ < Ni β < Znβ < Naβ.

2.3 Conclusions

1. X ray studies reveal that HPWA interacts strongly with zeolite supports in case of both HZSM-5(225) as well as HY zeolite as evident from the additional absorption peaks which are not observed in the pure catalysts.
2. In the composite catalysts of HPWA and HY, the Keggin structure bands of HPWA grow in intensity as the concentration of HPWA increases from 10 % to 40 % indicating that the bulk properties of HPAs prevail at higher loadings of HPWA on the support.
3. Y and β zeolites exhibited a much higher BET surface area as compared to ZSM-5 zeolites. HY exhibited the highest BET surface area among the various catalysts used in this investigation. HPWA had a very low BET surface area (11 m^2 / g). However the composite catalysts of HPWA with zeolite supports showed significantly higher BET surface areas. For the HPWA/HY composite catalysts of different compositions, the BET surface area decreased progressively with an increase in HPWA content.
4. Hβ was found to exhibit the highest total acidity among the zeoilte catalysts used in this investigation. HPWA was found to be more acidic than zeolites (Total acidity = 0.50115 mmol / g).
5. The composite catalysts of HPWA with HY zeolite showed variable acid strengths. The composite catalysts 10%HPWA/HY and 20%HPWA/HY showed a lower total acidity than both the individual catalysts, whereas the other two composite catalysts viz. 30%HPWA/HY and 40%HPWA/HY exhibited intermediate total acidity values compared to that of pure catalysts.

The reason for this could be the interaction of HPWA with the support. Owing to this interaction between HPWA and the zeolites additional acid sites may be generated or there may be modification of acid sites present in the pure catalysts.

6. The zeolite catalysts exhibited a high total acidity as compared to total basicity.

7. The sodium form possessed the highest total basicity in case of all the three kinds of zeolites. NaY zeolite was found to be the most basic catalyst among all the zeolite catalysts used in this investigation.

Chapter 3

Ammonolysis of n-butyl alcohol

Ammonolysis of n-butyl alcohol

This Chapter describes the catalytic activity of various catalysts for the synthesis of amines by the ammonolysis reaction of n-butyl alcohol with ammonia. The ammonolysis reaction of n-butyl alcohol is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia over ZSM-5, Y and β zeolites and phosphotungstic acid. 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 formation of undesirable products. The catalytic activity is correlated to the catalyst characteristics.

3.1 Reaction procedure

The ammonolysis of n-butyl alcohol was carried out in a vertical flow type of a reactor system as shown in Figure 3.1 at atmospheric pressure. In a typical experiment, 5 g of the catalyst in extrudate form is packed in a quartz reactor. The catalyst is activated in flowing air for about 6 hours at 500 °C. The temperature is then brought to the reaction temperature in dry nitrogen. The reactants n-butyl alcohol (Loba Chemie, India, commercial, distilled) and anhydrous ammonia (Bhoruka gases Pvt. Ltd., India, purity 99.8 %) are then passed through the reactor, from a Miclins syringe peristaltic 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 are mixed in a pre - heater cum mixer and then passed over the catalysts. The products are then analysed by gas chromatography with 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 are identified by GC-mass spectrometry and by chemical analysis. The products of the reaction were found to be the primary, secondary and tertiary amines i.e. n-butylamine (NBA), dibutylamine (DBA) and tributylamine (TBA) respectively, butyraldehyde (PrCHO) and butyronitrile (PrCN) and 1-butene.

The calculations for conversion and selectivity are expressed as follows:

Molar percentage conversion of alcohol (% C alcohol) = (Moles of alcohol converted to products / Moles of alcohol passed over the catalyst) X 100

Molar percentage selectivity to a product (% Product distribution) = (Moles of a product formed / Moles of alcohol converted) X 100

Total molar selectivity to amines (% S amines) = (Sum of moles of amines formed / Moles of alcohol converted) X 100

Percentage molar conversion of alcohol to amines (% C alcohol to amines) = (Molar percentage conversion of alcohol X Total molar selectivity to amines) / 100

Percentage selectivity to individual amines in a mixture of amines was also calculated in certain cases to study the relative proportion of an individual amine in a mixture of amines.

Percentage selectivity to an individual amine in a mixture of amines = (Molar percentage selectivity to the individual amine / Total molar selectivity to amines) X 100

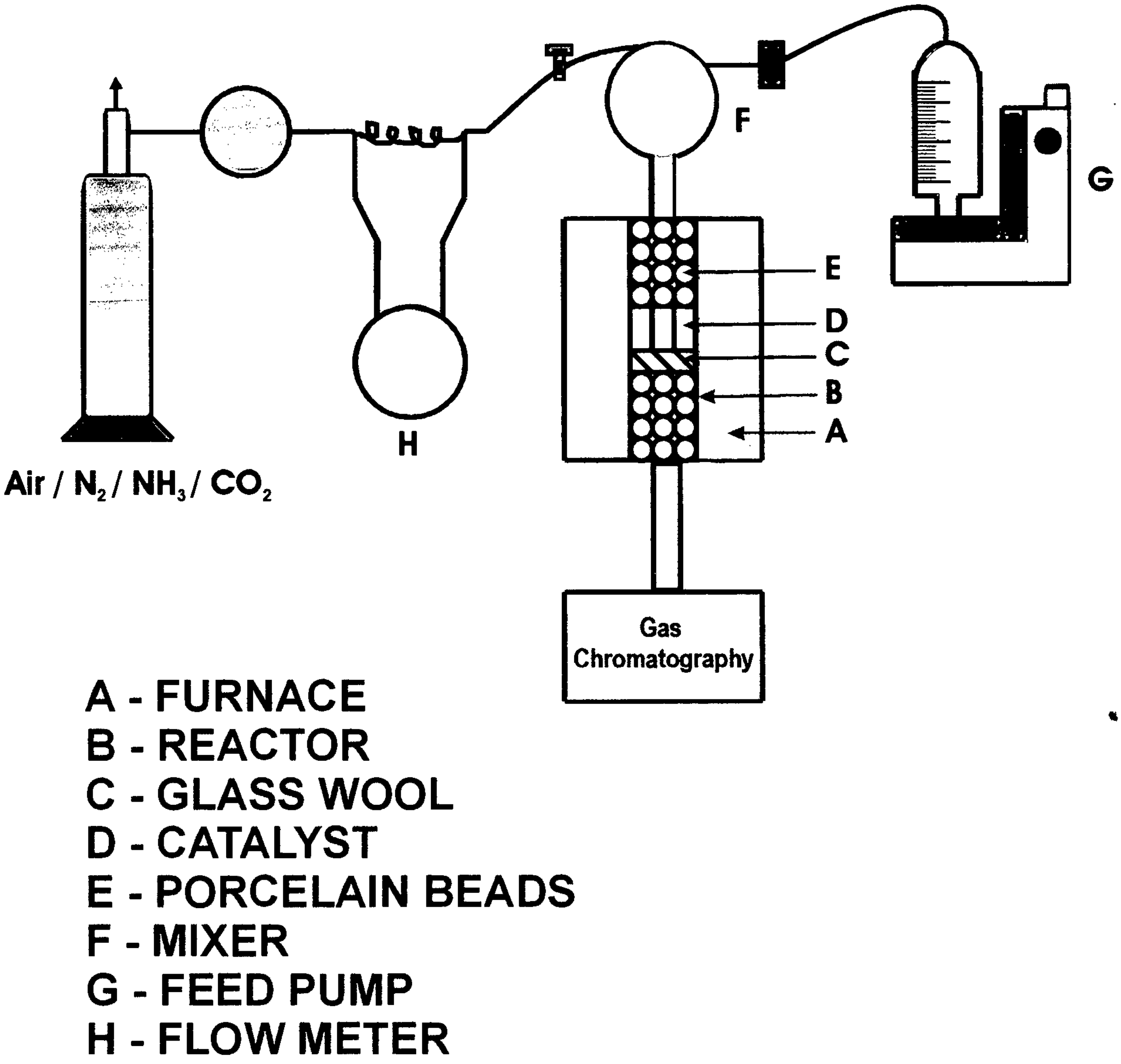

Fig. 3.1 Reaction setup.

3.2 Ammonolysis of n-butyl alcohol over ZSM-5 zeolite catalysts

HZSM-5(40) was taken as a model catalyst to optimise the conditions for the comparison of various catalysts. The effect of temperature on ammonolysis reaction of n-butyl alcohol at a LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4 over HZSM-5(40) is shown in Table 3.1.

Table 3.1 Effect of temperature on ammonolysis reaction of n-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
250	20.17	67.03	--	--	18.95	7.44	6.58	32.97	6.65
300	29.14	69.12	1.39	--	16.65	8.82	4.02	29.49	8.59
350	42.54	71.50	2.75	1.94	13.36	6.23	4.22	23.81	10.13
400	**66.58**	**54.77**	**1.79**	--	**25.57**	**10.54**	**7.33**	**43.44**	**28.92**
450	78.31	83.94	--	--	11.98	4.08	--	16.06	12.58

Reaction Conditions:
Weight of catalyst = 5g
LHSV = 1.00 h^{-1}
Molar ratio = 1:3
(alcohol : NH_3
TOS = 1h

% C alcohol - Molar percentage conversion of alcohol

% Product distribution - Molar percentage selectivity to different products

% S amines - Total molar percentage selectivity to amines

% C alcohol to amines - Percentage molar conversion of alcohol to amines

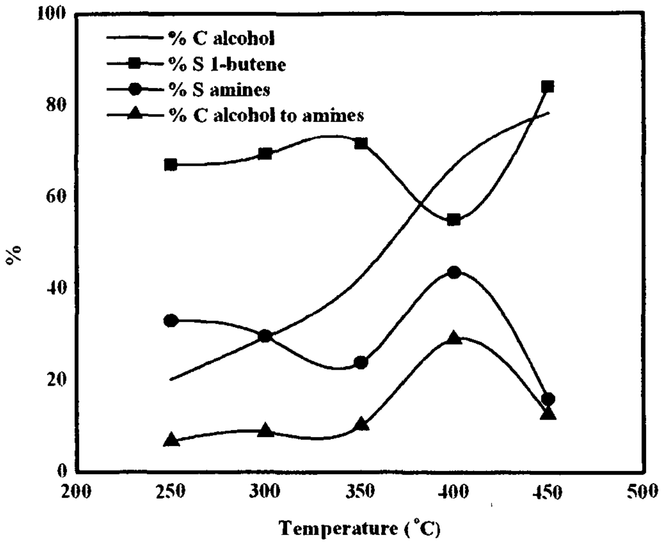

Figure 3.2 Effect of temperature on ammonolysis reaction of n-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g	LHSV = 1.00 h^{-1}
Molar ratio (alcohol : NH_3) = 1 : 4	TOS = 1 h

It is observed that the protonic zeolite shows a high selectivity for the dehydration of alcohol to give 1-butene. At low temperatures below 350 °C the conversion of alcohol is very low. With increase in temperature the conversion of alcohol increases however the highest yield is obtained at a temperature of 400 °C where in ~ 29 % of alcohol is converted into amines. At very high temperature, i.e. 450 °C the dehydration activity is very high thereby lowering the selectivity to amines. The other side products for the reaction are butyraldehyde formed by the dehydrogenation of alcohol and butyronitrile. It should be noted that nitrile is considered to be the principal product in ammonolysis reactions of alcohols in certain studies over different catalysts [10, 68, 69]. However in present studies, the focus is on the synthesis of amines and hence, butyronitrile is considered to be a side - product. The reaction was further investigated for LHSV variations over HZSM-5(40) zeolite at a temperature of 400 °C and an alcohol to ammonia molar ratio of 1 : 4.

Table 3.2 shows that the effect of LHSV on ammonolysis reaction of n-butyl alcohol over HZSM-5(40) zeolite.

Table 3.2 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
0.50	69.52	70.91	--	--	9.95	11.04	8.10	29.09	20.22
0.75	67.93	64.35	1.90	--	15.84	10.97	6.94	33.75	22.93
1.00	**66.58**	**54.77**	**1.79**	--	**25.57**	**10.54**	**7.33**	**43.44**	**28.92**
1.25	58.72	55.11	1.36	1.74	25.97	9.54	6.28	41.79	24.54
1.50	49.18	58.48	1.89	--	26.88	7.54	5.21	39.63	19.49
1.75	44.39	59.68	1.46	--	28.09	10.77	--	38.86	17.25

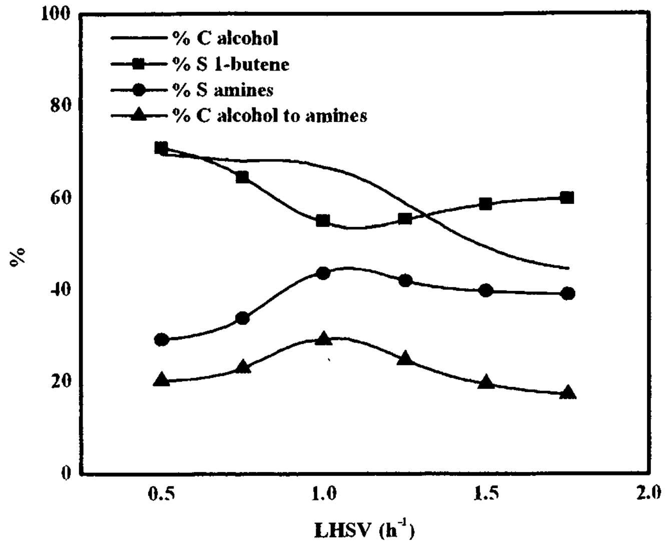

Figure 3.3 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g	Temperature = 400 °C
Molar ratio (alcohol : NH_3) = 1 : 4	TOS = 1 h

The conversion of n-butyl alcohol decreases with increase in LHSV from 0.50 h^{-1} to 1.75 h^{-1}. This is as expected as the contact time of the reactants over the catalyst is lowered as LHSV is increased. However, the selectivity to amines shows a different pattern. The highest conversion of alcohol to amines is obtained at a LHSV of 1.00 h^{-1}.

The reaction was further investigated for alcohol to ammonia molar ratio variations. The data is presented in Table 3.3.

Table 3.3 Effect of molar ratio on ammonolysis reaction of n-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
1 : 3	64.17	54.80	1.98	1.88	21.48	10.92	8.94	41.34	26.53
1 : 4	**66.58**	**54.77**	**1.79**	**--**	**25.57**	**10.54**	**7.33**	**43.44**	**28.92**
1 : 5	59.12	56.84	1.08	1.35	33.17	6.52	1.04	40.73	24.08
1 : 6	43.18	55.61	--	--	39.45	4.94	--	44.39	19.17

Thus over HZSM-5(40) zeolite, the highest conversion of alcohol to amines is obtained at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4. The catalytic activity of the different ZSM-5zeolite catalysts was evaluated under this condition. The data is presented in **Table 3.4**.

Table 3.4 Catalytic activity of ZSM-5 zeolite catalysts for the ammonolysis reaction of n-butyl alcohol.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Catalyst	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
HZSM-5(40)	66.58	54.77	1.79	--	25.57	10.54	7.33	43.44	28.92
HZSM-5(80)	64.56	50.28	1.28	1.85	26.93	12.18	7.48	46.59	30.08
HZSM-5(225)	**61.05**	**42.58**	**1.83**	**1.36**	**35.08**	**11.79**	**7.36**	**54.23**	**33.11**
NaZSM-5	24.68	73.88	2.33	--	12.54	7.36	3.89	23.79	5.87
CuZSM-5	35.76	56.29	2.76	1.64	14.54	13.27	11.50	39.31	14.05
NiZSM-5	39.23	60.50	2.09	1.27	18.71	10.44	6.99	36.14	14.17
ZnZSM-5	37.13	59.46	2.98	--	18.64	11.56	7.36	37.56	13.94

It is observed from Table 3.4 that the HZSM-5 zeolites show a high activity for the conversion of n-butyl alcohol (> 60 %). The conversion of alcohol to amines is ~ 30 %, the remaining products being mainly the dehydration product 1-butene and little of dehydrogenation product, i. e. butyraldehyde and butyronitrile. The variation of Si/Al ratio of HZSM-5 zeolite has a pronounced effect on the catalytic activity. For the three different HZSM-5 zeolite viz. HZSM-5(40), HZSM-5(80) and HZSM-5(225), it is observed that the percentage conversion of alcohol decreases as the Si/Al ratio increases (decreasing activity). This decreasing conversion of alcohol is accompanied by a decreased formation of 1-butene thus suggesting a lower intramolecular dehydration. However, the selectivity towards amines and the molar percentage conversion of alcohol to amines increased significantly with an increase in Si/Al ratio. This could be attributed to direct intermolecular dehydration between the alcohol and ammonia over the less acidic HZSM-5(225) zeolite. However the TPD profiles of HZSM-5 zeolites shown in Figure 2.14 suggest that ammonia gets desorbed from the catalyst surface beyond 400 °C. Therefore it is unlikely that the above ammonolysis process occurs between the two co-adsorbed reactants. Therefore ammonolysis under these conditions could occur through Eley – Rideal type mechanism wherein the ammonia from gas phase could collide with the adsorbed alcohol to yield the butylamines. Thus the TPD profiles are useful not only to characterize the acid sites but also the state of ammonia (free or adsorbed on the catalyst surface) for the ammonolysis reaction.

Table 3.5 shows the comparative catalytic activity of HZSM-5 zeolites of different Si/Al ratios and their corresponding total acidity and total basicity.

Table 3.5 Catalytic activity of HZSM-5 zeolites of different Si/Al ratios and their corresponding total acidity and total basicity.

Catalyst	% C alcohol	%S 1-butene	% S amines	% C alcohol to amines	Total acidity (mmol / g)	Total basicity (μmol / g)
HZSM-5(40)	66.58	54.77	43.44	28.92	0.47371	0.01547
HZSM-5(80)	64.56	50.28	46.59	30.08	0.23446	0.02850
HZSM-5(225)	61.05	42.58	54.23	33.11	0.06964	0.04189

It can be seen from the Table 3.5 that acidity and basicity play a crucial role in the catalytic activity. Decreasing total acidity resulted in a lowered conversion of alcohol. However, it is observed the conversion of alcohol to amines is enhanced. This could be attributed to the decreasing selectivity to intramolecular dehydration product i.e. 1-butene over the less acidic HZSM-5 zeolite. The most active catalyst for the above reaction, i. e. HZSM-5(225) zeolite has a low total acidity and a high total basicity. Thus, in case of HZSM-5 zeolite catalysts, it is observed that HZSM-5 zeolite with a low total acidity and a high total basicity favours the synthesis of butylamines by the reaction of n-butyl alcohol and ammonia [290].

The other ZSM-5 zeolites, i.e. NaZSM-5, CuZSM-5, NiZSM-5 and ZnZSM-5 showed a very low activity for the conversion of alcohol to amines. The loss of selectivity towards amines is due to high dehydration activity over these catalysts to yield 1-butene.

Thus HZSM-5(225) was the most active catalyst among various ZSM-5 zeolite catalysts screened in the initial investigations. The reaction was further investigated over HZSM-5(225) for temperature, LHSV and alcohol to ammonia molar ratio variations to optimise the conditions to obtain the best yields of amines.

Table 3.6 shows the effect of temperature on the ammonolysis reaction over HZSM-5(225) zeolite.

Table 3.6 Effect of temperature on ammonolysis reaction of n-butyl alcohol over HZSM-5(225) zeolite.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
300	37.58	53.18	1.16	2.95	25.42	11.18	6.11	42.71	16.05
350	46.42	39.90	4.85	2.78	27.93	15.12	9.42	52.47	24.36
400	**61.05**	**42.58**	**1.83**	**1.36**	**35.08**	**11.79**	**7.36**	**54.23**	**33.11**
450	74.16	75.15	--	--	18.68	6.17	--	24.85	18.43

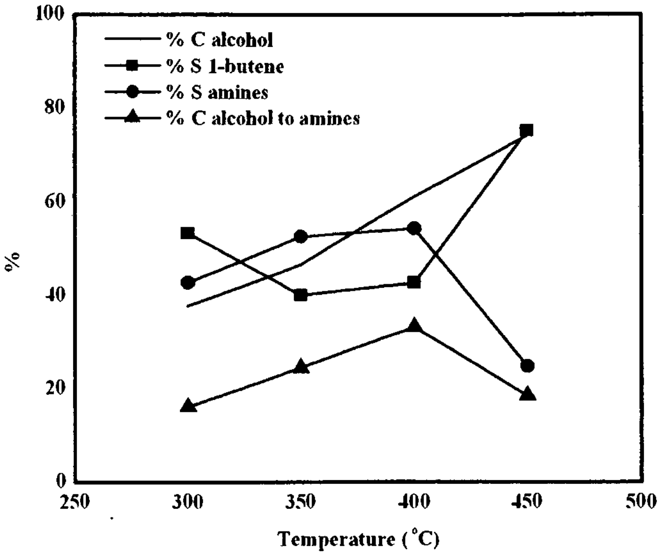

Figure 3.4 Effect of temperature on ammonolysis reaction of n-butyl alcohol over HZSM-5(225) zeolite.

Weight of catalyst = 5 g   LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4   TOS = 1 h

The percentage conversion of alcohol increases with temperature however the conversion of alcohol to amines is highest at a temperature of 400 °C. At 450 °C, a high percentage of n-butyl alcohol is converted to 1-butene resulting in a lowered selectivity towards amines. The primary amine was the major product at all temperatures (> 50 % selectivity). At higher temperatures the primary amine formed may be desorbed at a faster rate, which may prevent further alkylation of primary amine with alcohol as per reactions (2) and (3) as shown previously, thereby, reducing the yields of secondary and tertiary amines. Thus at higher temperatures the probability of the alkylation of the primary amine is lowered considerably thereby decreasing the selectivity towards the secondary and tertiary amines.

The effect of LHSV on the ammonolysis reaction over HZSM-5(225) zeolite is shown in Table 3.7.

Table 3.7 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over HZSM-5(225) zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
0.25	67.28	55.49	1.32	2.68	15.12	14.57	10.82	40.51	27.26
0.50	66.92	53.42	2.83	--	19.62	14.08	10.05	43.75	29.28
0.75	63.75	46.50	1.99	2.43	26.54	13.71	8.83	49.08	31.29
1.00	61.05	41.58	1.83	2.36	35.08	11.79	7.36	54.23	33.11
1.25	**60.74**	**16.71**	**3.22**	**1.89**	**55.33**	**14.88**	**7.97**	**78.18**	**47.48**
1.50	59.38	25.81	2.92	1.72	49.94	13.03	6.58	69.55	41.30
1.75	56.47	30.44	3.40	--	49.85	11.13	5.18	66.16	37.36
2.00	52.09	39.90	3.17	--	44.26	8.72	3.95	56.93	29.65

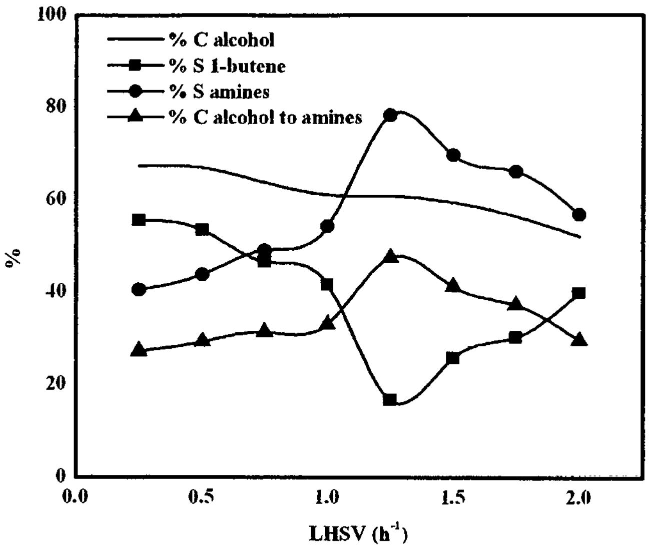

Figure 3.5 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over HZSM-5(225) zeolite.

Weight of catalyst = 5 g   Temperature = 400 °C

Molar ratio (alcohol : NH_3) = 1 : 4   TOS = 1 h

The highest conversion of alcohol to amines is obtained at a LHSV of 1.25 h^{-1}. Although the conversion decreases from 61.75 % at 1.00 h^{-1} to 59.38 % at 1.50 h^{-1} the selectivity to amines increases considerably. This is attributed to a lowered selectivity towards the dehydration product. It is also observed that the increasing LHSV again results in an increased selectivity towards the primary amine, which may be attributed to a shorter contact time of the reactants over the catalyst.

Table 3.8 shows the effect of alcohol to ammonia molar ratio variations on the ammonolysis reaction over HZSM-5(225) zeolite.

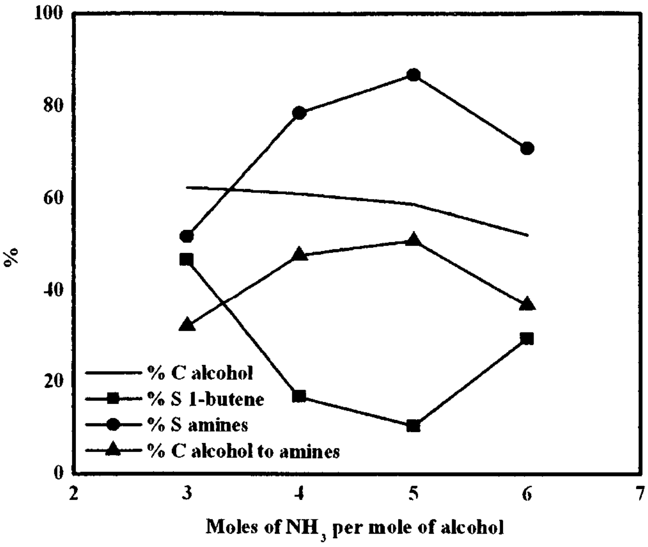

Figure 3.6 Effect of molar ratio on ammonolysis reaction of n-butyl alcohol over HZSM-5(225) zeolite.

Weight of catalyst = 5 g Temperature = 400 °C

LHSV = 1.25 h^{-1} TOS = 1 h

It is observed that although the conversion of n-butyl alcohol shows a decrease with an increase in ammonia content, the conversion of alcohol to amines follows a different pattern. The highest conversion of alcohol to amines is obtained at an alcohol to ammonia molar ratio of 1 : 5. Under this condition ~ 50 % of alcohol is converted to amines. No formation of butyronitrile was observed under this condition. It is observed that the alcohol to ammonia molar ratio variation also affects the selectivity towards individual amines. The selectivity towards n-butylamine is found to increase with an increase in alcohol to ammonia molar ratio, from 1 : 3 to 1 : 5. This increased selectivity towards primary amine at higher alcohol to ammonia ratios has been reported previously [137]. At higher molar ratio however i.e. at 1 : 6 no significant difference is observed towards the selectivity towards individual amines and also the conversion of alcohol to amines becomes low under this condition. Thus the best yields over HZSM-5(225) were obtained at a temperature of 400 °C, LHSV of 1.25 h^{-1} and an alcohol to ammonia molar ratio of 1 : 5. At this condition ~ 50 % of alcohol is converted to amines with a very high selectivity ~ 85 % towards amines out of which ~ 63 % was n-butylamine Time on stream studies were carried out on the HZSM-5(225) zeolite at these conditions to study the activity of the catalyst over a period of time. The data is presented in Figure 3.7.

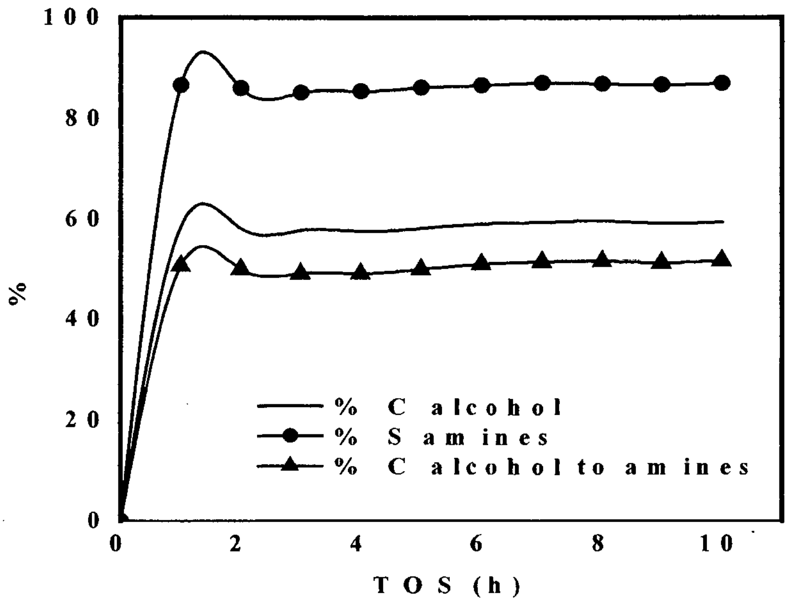

Figure 3.7 Time on stream studies over HZSM-5(225) zeolite.

Weight of catalyst = 5 g Temperature = 400 °C

LHSV = 1.25 h^{-1} Molar Ratio (alcohol : NH_3) = 1 : 5

The catalyst showed a steady performance over a period of 10 hours. The conversion of alcohol and the conversion of alcohol to amines showed a little decrease up to the fourth hour, however the catalyst regained the original activity after the fourth hour. The activity is then maintained over a period of 10 hours. This is in accordance with the non-coking properties of ZSM-5 zeolite [73]. Thus HZSM-5(225) was found to be a highly active catalyst showing ~ 50 % conversion to amines with a high selectivity towards n-butylamine.

3.3 Ammonolysis of n-butyl alcohol over Y zeolite catalysts

The catalytic activity of various Y zeolite catalysts was determined at the preoptimised temperature of 400 °C, LHSV of 1.00 h^{-1} and alcohol to ammonia molar ratio of 1 : 4. The data is shown in Table 3.9.

Table 3.9 Catalytic activity of various Y zeolite catalysts for the ammonolysis reaction of n-butyl alcohol.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Catalyst	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
NaY	19.56	64.02	6.23	--	13.85	8.42	7.48	29.75	5.82
HY	**52.12**	**64.83**	**--**	**--**	**14.43**	**10.76**	**9.88**	**35.07**	**18.27**
CuY	49.89	72.44	2.48	2.14	15.76	7.18	--	22.94	11.44
NiY	48.95	73.05	1.97	--	16.36	8.62	--	24.98	12.23
ZnY	39.73	67.89	1.93	--	13.75	9.82	6.61	30.18	12.22

Among the Y zeolites, the protonic zeolite, i.e. HY zeolite shows the highest conversion of alcohol (~ 52 %) however the conversion of alcohol to amines was very low (~18 %) due to a very high dehydration activity (~ 65 %) to yield 1-butene. The activity for the formation of amines was found to be very low compared to that of

HZSM-5 zeolites. NaY showed a poor catalytic activity in contrast to the reported literature [7]. The other three Y zeolites i. e. CuY, NiY and ZnY also exhibited a poor catalytic activity for the formation of amines (~ 12 % conversion of alcohol to amines). Thus Y zeolites proved to be less active for the ammonolysis reaction of n-butyl alcohol.

3.4 Ammonolysis of n-butyl alcohol over β zeolite catalysts

The catalytic activity of various β zeolite catalysts was determined at the preoptimised temperature of 400 °C , LHSV of 1.00 h^{-1} and alcohol to ammonia molar ratio of 1 : 4.

Table 3.10 Catalytic activity of various β zeolite catalysts for the ammonolysis reaction of n-butyl alcohol.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Catalyst	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
Naβ	**41.32**	**36.83**	**3.48**	**1.36**	**30.08**	**17.54**	**10.71**	**58.33**	**24.10**
Hβ	58.19	72.30	--	--	16.98	10.72	--	27.70	16.12
Cuβ	48.05	68.75	1.68	2.74	21.04	5.79	--	26.83	12.89
Niβ	36.53	71.52	--	--	16.46	7.83	5.19	29.48	10.77
Znβ	35.93	77.52	2.95	2.01	10.98	6.54	--	17.52	6.29

In the case of the β zeolites, the sodium form i.e. Naβ zeolite showed a high catalytic activity. Hβ and Cuβ show a catalytic activity similar to that of HY, a high conversion of alcohol but a low yield of amines due to high selectivity towards 1-butene. It is seen that the protonic form Hβ showed a higher conversion of alcohol than Naβ zeolite. This high conversion however resulted mainly in dehydration (~ 72

%) to yield 1-butene. Hβ zeolite also did not show any dehydrogenation activity. On the other hand, Naβ zeolite showed a small amount of dehydrogenation activity (~ 5 %) as evident from the formation of butyraldehyde or butyronitrile. In comparison, the dehydration activity of Naβ was much lower (~ 36 %). This was accompanied by a high selectivity towards amines (~ 58 %). However, the catalysts Cuβ, Niβ and Znβ, which showed high dehydration, did not show high selectivity to amines like Hβ. 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 $H\text{-}NH_2$ to carbon – carbon double bond; but formation of sec-butylamine was not observed. Ammonolysis thus could probably occur by direct intermolecular dehydration between alcohol and ammonia.

$$n\text{-}CH_3CH_2CH_2CH_2OH + NH_3 \rightarrow n\text{-}CH_3CH_2CH_2CH_2NH_2 + H_2O \text{ -------(1)}$$

TPD profiles of adsorbed ammonia shown in Figure 2.19 indicate that no substantial ammonia should be present on the catalysts in the adsorbed state at temperatures beyond 400 °C. Hence it is believed that the reaction (1) occurs via Eley - Rideal mechanism involving interaction between gas phase ammonia and adsorbed alcohol [291].

Thus Naβ was the most active catalyst among various β zeolite catalysts screened. Further optimisation of reaction parameters was carried out to improve the selectivity to amines over Naβ zeolite Table 3.11 shows the effect of temperature on the ammonolysis reaction of n-butyl alcohol over Naβ zeolite.

Table 3.11 Effect of temperature on ammonolysis reaction of n-butyl alcohol over Naβ zeolite.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
350	48.16	43.15	3.15	1.57	22.60	18.54	10.99	52.13	25.10
400	51.32	36.83	3.48	1.36	30.08	17.54	10.71	58.33	29.93
450	**58.97**	**30.72**	**5.67**	**2.52**	**36.92**	**15.13**	**9.04**	**61.09**	**36.02**
480	64.16	51.38	--	--	38.17	6.54	3.91	48.62	31.19

The percentage conversion of alcohol increases as the temperature is increased from 350 °C to 480 °C. However at 480 °C, the percentage dehydration was the highest (~ 51 % 1-butene formation). This, as mentioned above, is not desirable for getting higher yields of amines. On the other hand, at 450 °C, 1-butene formed was minimum (~ 30 %). As expected, the percentage molar conversion of alcohol to amines was higher with ~ 61 % selectivity to amines. Figure 3.8 describes the pattern of selectivity to individual amines from the mixture of three amines.

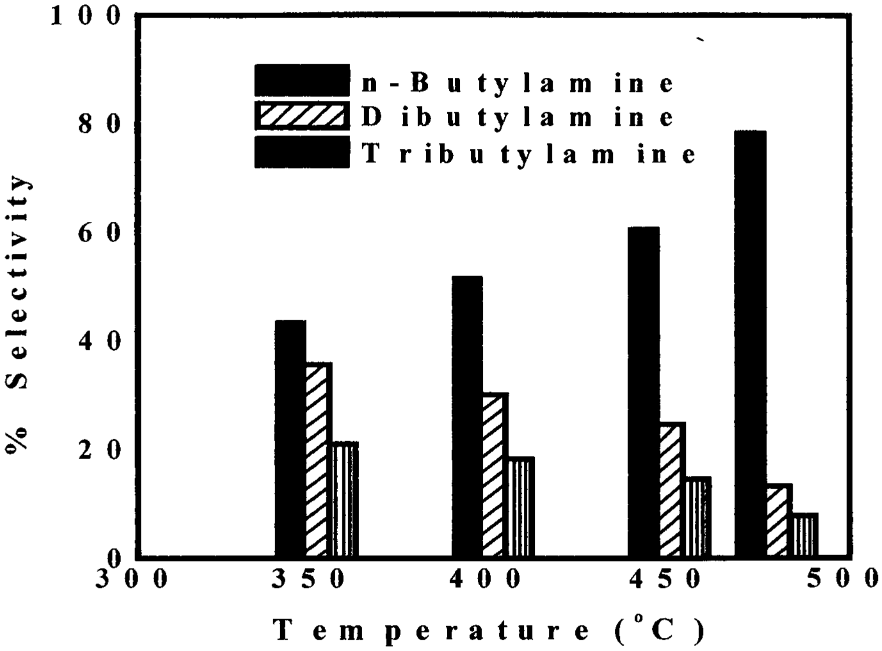

Figure 3.8 Percentage selectivity to individual amines in a mixture of amines at different temperatures over Naβ zeolite.

Weight of catalyst = 5 g	LHSV = 1.00 h^{-1}
Molar ratio (alcohol : NH_3) = 1 : 4	TOS = 1 h

It was observed that the selectivity to primary amine increased as the temperature is increased. At the same time the 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 of the primary amine to secondary or tertiary amines as per reactions (2) and (3).

$CH_3CH_2CH_2CH_2NH_2$ + n-$CH_3CH_2CH_2CH_2OH \rightarrow (CH_3CH_2CH_2CH_2)_2NH + H_2O$--(2)

$(CH_3CH_2CH_2CH_2)_2NH$ + n-$CH_3CH_2CH_2CH_2OH \rightarrow (CH_3CH_2CH_2CH_2)_3N + H_2O$--(3)

Further investigation of this aspect was carried out by studying the effect of flow rate flow rate of the reactants (LHSV variations) at a temperature of 450 °C as shown in Table 3.12.

Table 3.12 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over Naβ zeolite.

Weight of catalyst = 5 g

Temperature = 450 °C

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
0.50	64.07	33.06	6.02	3.54	12.15	20.18	25.05	57.38	36.76
0.75	**61.94**	**26.26**	**5.82**	**2.65**	**8.12**	**46.13**	**11.02**	**65.27**	**40.42**
1.00	58.97	30.72	5.67	2.52	36.92	15.13	9.04	61.09	36.02
1.50	54.32	39.03	4.95	1.85	33.60	11.95	8.62	54.17	29.42
2.00	50.17	44.75	4.88	1.04	34.97	14.36	--	49.33	24.74

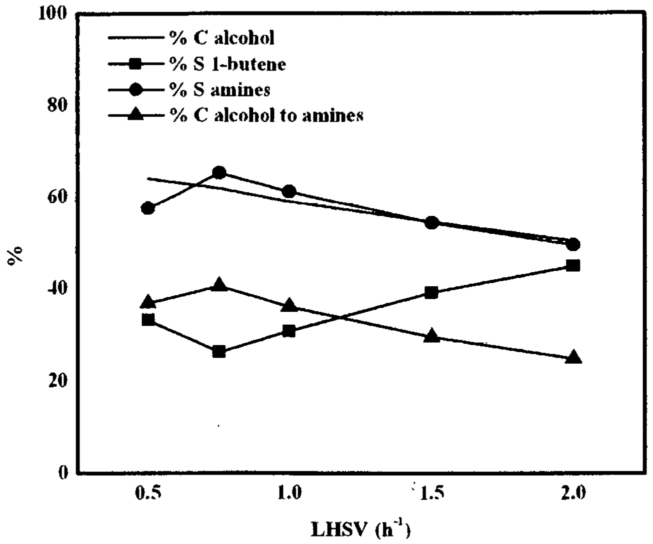

Figure 3.9 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over Naβ zeolite.

Weight of catalyst = 5 g Temperature = 450 °C

Molar ratio (alcohol : NH_3) = 1 : 4 TOS = 1 h

It can be seen that as the LHSV is increased from 0.50 h^{-1} to 1.00 h^{-1}, the selectivity pattern greatly changes. Thus at a very low LHSV of 0.50 h^{-1}, the catalyst is predominantly selective to tributylamine. At a LHSV of 0.75 h^{-1}, a large selectivity is observed for dibutylamine (~ 46 %) while the selectivity towards tributylamine decreased from 25 % to 11 %. At a still higher LHSV of 1.00 h^{-1}, the catalyst showed a higher selectivity towards n-butylamine at the cost of di- and tri- 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 [84]. Thus, the contact time of the reactants over the catalyst surface 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 3.13.

Table 3.13 Effect of molar ratio of on ammonolysis reaction of n-butyl alcohol over Naß zeolite.

Weight of catalyst = 5 g

Temperature = 450 °C

LHSV = 0.75 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
1 : 2	71.06	47.88	--	--	--	36.48	15.64	52.12	37.03
1 : 3	**66.08**	**30.82**	--	--	**1.67**	**55.43**	**12.08**	**69.18**	**45.71**
1 : 4	61.94	26.26	5.82	2.65	8.12	46.13	11.02	65.27	40.42
1 : 5	60.73	22.00	4.21	2.36	42.19	17.48	10.76	70.43	42.77
1 : 6	61.04	31.23	3.49	1.58	54.02	9.68	--	63.70	38.88

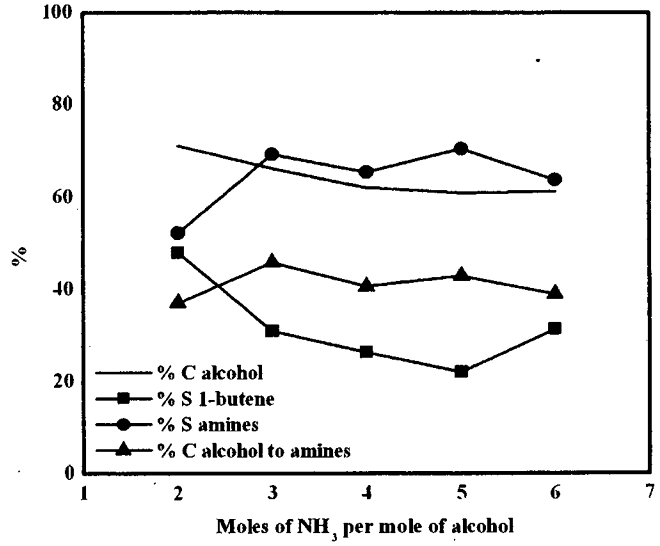

Figure 310 Effect of molar ratio of on ammonolysis reaction of n-butyl alcohol over Naß zeolite.

Weight of catalyst = 5 g Temperature = 450 °C

LHSV = 0.75 h^{-1} TOS = 1 h

A high conversion ~ 66 % with relatively low 1-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 is increased the primary amine formation increased to ~ 54 % while the secondary amine formation decreased to a low ~ 10 % at 1 : 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} and a temperature of 450 °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} and a temperature of 450 °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 Naβ zeolite at a temperature of 450 °C, LHSV of 0.75 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 3. The data is presented in Figure 3.11.

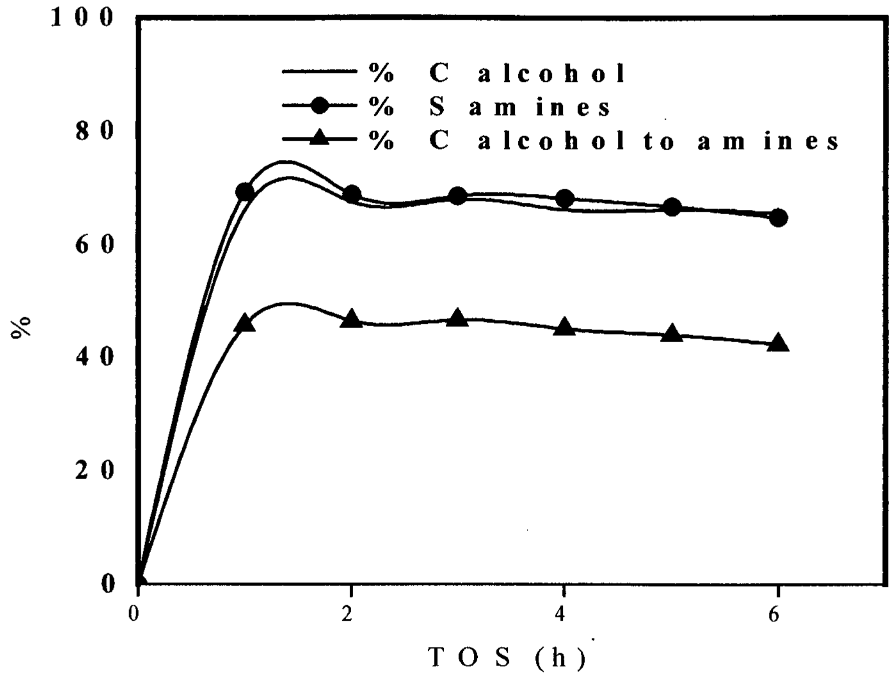

Figure 3.11 Time on stream studies over Naβ zeolite.

Weight of catalyst = 5 g Temperature = 450 °C

LHSV = 0.75 h^{-1} 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. ~ 42 % of alcohol is converted to amines by the sixth hour.

Figure 3.12 shows the pattern of selectivity to individual amines in a mixture of amines at different TOS over Naβ zeolite.

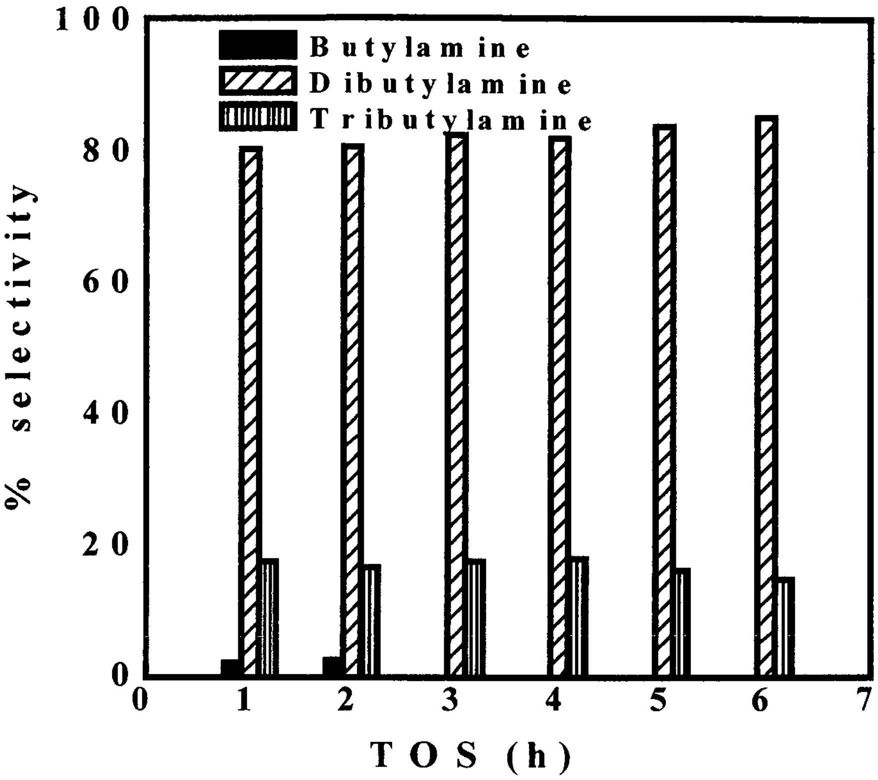

Figure 3.12 Percentage selectivity to individual amines at different TOS over Naβ zeolite.

Weight of catalyst = 5 g　　Temperature = 450 °C

LHSV = 0.75 h^{-1}　　Molar ratio (alcohol : NH_3) = 1 : 3

It can be seen from Figure 3.12 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 Naβ zeolite can be used to obtain dibutylamine with high selectivity at optimum conversion of alcohol.

3.5 Ammonolysis of n-butyl alcohol over phosphotungstic acid (HPWA)

Heteropoly acids have been found to be attractive catalysts for various heterogenous catalytic reactions mainly because of their acidic properties and ability to catalyse oxidation reactions. Heteropoly acids have been used to catalyse the dehydration reactions of alcohol [292, 293]. Since the ammonolysis reaction of alcohols also involves the intermolecular dehydration, the heteropoly acids are likely to have a good potential for the ammonolysis reactions of alcohols. The catalytic activity of phosphotungstic acid (HPWA), the strongest acid among heteropoly acids was tested for the ammonolysis reaction of n-butyl alcohol. The reaction as before was investigated over HPWA as a function of temperature, LHSV and alcohol to ammonia molar ratio variations.

The effect of temperature on ammonolysis reaction of n-butyl alcohol over phosphotungstic acid is shown in Table 3.14.

Table 3.14 Effect of temperature on ammonolysis reaction of n-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
300	69.82	82.27	1.02	1.59	4.92	8.62	1.58	15.12	10.55
350	**72.05**	**60.48**	**1.58**	**1.77**	**23.93**	**10.08**	**2.16**	**36.17**	**26.06**
400	78.32	81.12	--	--	10.63	8.25	--	18.88	14.78
450	84.18	87.36	--	--	12.64	--	--	12.64	10.64

It is observed that the over HPWA showed very high conversions of alcohol (~ 85 % at a temperature of 450 °C), but the selectivity to amines is lowered due to a high dehydration activity. The highest conversion of alcohol to amines is obtained at a temperature of 350 °C where in ~ 26 % of the alcohol is converted into amines. The reaction was further investigated for LHSV variations. The data is presented in Table 3.15.

Table 3.15 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

Temperature = 350 °C

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
0.50	78.13	56.69	1.62	1.61	10.35	18.06	11.67	40.08	31.31
1.00	72.05	60.48	1.58	1.77	23.93	10.08	2.16	36.17	26.06
1.50	**68.18**	**43.05**	**2.52**	**--**	**36.03**	**12.76**	**5.64**	**54.43**	**37.11**
2.00	64.03	60.46	--	--	29.68	9.86	--	39.54	25.32

At lower LHSVs the conversion of n-butyl alcohol is high, however the highest conversion of alcohol to amines is obtained at a LHSV of 1.50 h^{-1}. It can be seen that with increasing LHSV the selectivity to primary amine increases and at lower LHSV the secondary and tertiary amines are obtained with higher selectivities at the expense of primary amine.

The effect of alcohol to ammonia molar ratio on the ammonolysis reaction of n-butyl alcohol over HPWA catalyst is shown in Table 3.16.

Table 3.16 Effect of molar ratio on ammonolysis reaction of n-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

Temperature = 350 °C

LHSV = 1.50 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
1 : 3	64.78	57.11	1.82	--	20.33	15.06	5.68	41.07	26.02
1 : 4	**68.18**	**43.05**	**2.52**	**--**	**47.03**	**7.40**	**--**	**54.43**	**37.11**
1 : 5	65.93	41.42	2.54	--	47.95	8.07	--	56.02	36.93
1 : 6	62.48	51.29	--	--	45.03	3.68	--	48.71	30.43

The best yields over HPWA catalyst was obtained at a temperature of 350 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4 where in ~ 37 % conversion of alcohol to amines was obtained with a high selectivity towards n-butylamine and with no formation of tributylamine.

3.6 Ammonolysis of n-butyl alcohol over 20%HPWA/HZSM-5(225) composite catalyst

From the results on the catalysts HZSM-5(225) and HPWA, it is evident that the reaction conditions that yielded low dehydration product, resulted in a high selectivity to amines. Further HPWA also tended to cause high conversion activity. Therefore a composite catalyst of HPWA and HZSM-5(225) was prepared to investigate the ammonolysis reaction.

A 20%HPWA/HZSM-5(225) catalyst formulation was thus prepared in the present investigation. The acidity of the catalyst was evaluated using TPD of NH_3 and it was observed that the acidity of composite catalyst was different from that of the pure catalysts as can be seen from Figure 2.21. The catalytic activity of the composite catalyst was evaluated for the ammonolysis reaction of n-butyl alcohol. The catalytic activity of the composite catalyst was evaluated for the ammonolysis reaction of n-butyl alcohol. The reaction was investigated over the composite catalyst 20% HPWA/HZSM-5(225) as a function of temperature, LHSV and alcohol to ammonia molar ratio variations.

The effect of temperature on the ammonolysis reaction of n-butyl alcohol over 20% HPWA/HZSM-5(225) at a LHSV of 1.50 h^{-1} and molar ratio of alcohol : NH_3 of 1 : 4 is shown in Table 3.17.

Table 3.17 Effect of temperature on ammonolysis reaction of n-butyl alcohol over 20%HPWA/HZSM-5(225) catalyst.

Weight of catalyst = 5 g

LHSV = 1.50 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
350	71.02	50.10	1.36	1.80	23.19	14.58	8.93	46.74	33.19
400	**78.02**	**33.17**	**1.89**	**1.57**	**39.98**	**14.65**	**8.74**	**63.37**	**49.44**
450	83.19	55.00	--	--	31.12	11.95	1.93	45.00	37.43

The synergistic effect was immediately evident as the composite catalyst resulted in high conversions of alcohol to amines in relation to the conversions obtained for the individual catalysts i. e. HZSM-5(225) and HPWA. Further at 400 °C, the dehydration activity was minimum and as expected from the previous trends the percentage conversion of alcohol to amines was highest i. e. ~ 49 %. A higher selectivity to primary amines was observed at higher temperatures.

The reaction was further investigated for LHSV variations over 20%HPWA/HZSM-5(225) catalyst . The data is shown in Table 3.18.

Table 3.18 Effect of LHSV on ammonolysis reaction of n-butyl alcohol over 20%HPWA/HZSM-5(225) catalyst.

Weight of catalyst = 5 g

Temperature = 400 °C

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
0.50	88.37	31.52	--	--	26.42	24.09	17.97	68.48	60.51
1.00	**84.96**	**15.78**	--	--	**48.03**	**21.38**	**14.81**	**84.22**	**71.55**
1.50	78.02	35.17	1.46	--	39.98	14.65	8.74	63.37	49.44
2.00	73.14	41.56	2.20	--	39.04	11.17	5.93	56.14	41.06

It is observed that the highest conversion of alcohol to amines is obtained at a LHSV of 1.00 h^{-1}, the only side product being 1-butene. It is interesting to note that under this condition, the selectivity towards amines rose to ~ 85 % at ~ 85 % conversion of alcohol.

The selectivity to individual amine in a mixture of amines is shown in Figure 3.13.

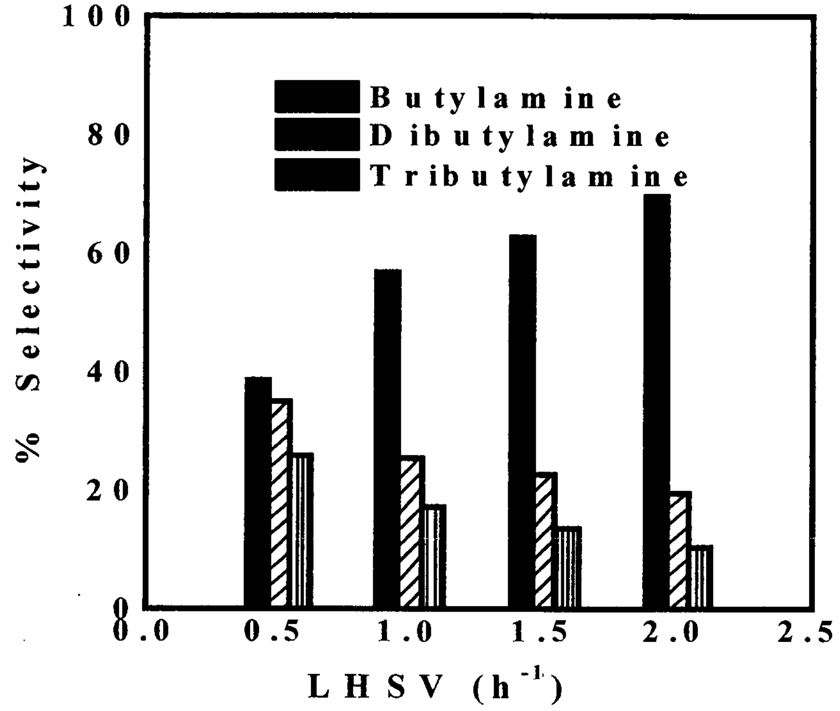

Figure 3.13 Percentage selectivity to individual amines in a mixture of amines at different LHSVs over 20%HPWA/HZSM-5(225) catalyst.

Weight of catalyst = 5 g
Temperature = 400 °C
Molar ratio (alcohol : NH_3) = 1 : 4
TOS = 1 h

It is observed that with increasing LHSV the proportion of primary amine increases. Thus when the reactants spend a shorter time on the catalyst (high LHSV), as expected the probability of further alkylation of primary amine to form secondary and tertiary amines is low. Hence there is predominant selectivity towards n-butylamine at higher LHSV. At lower LHSVs, the secondary and tertiary amines are formed at the expense of primary amine.

Further investigation was carried out to study the effect of molar ratio of alcohol to NH_3 on the ammonolysis reaction over the composite catalyst at a temperature of 400 °C and a LHSV of 1.00 h^{-1}. The data is presented in Table 3.19.

Table 3.19 Effect of molar ratio on ammonolysis reaction of n-butyl alcohol over 20%HPWA/HZSM-5(225) catalyst.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution						% S amines	% C alcohol to amines
		1-Butene	PrCHO	PrCN	NBA	DBA	TBA		
1 : 3	86.19	31.30	--	--	33.95	26.08	8.67	68.70	59.21
1 : 4	84.96	15.78	--	--	48.03	21.38	14.81	84.22	71.55
1 : 5	**81.54**	**11.38**	--	--	**77.25**	**11.37**	--	**88.62**	**72.26**
1 : 6	72.95	35.86	--	--	59.42	4.72	--	64.14	46.79

It is observed that nearly 88 % selectivity to amines is obtained at a molar ratio of 1 : 5 at a high conversion of alcohol (~ 80 %) such that ~ 72 % of alcohol is converted to amines. This is attributed to the facilitation of the ammonolysis reaction of alcohol to a high extent such that dehydration activity of alcohol to give 1-butene is very low (~ 11 % selectivity) and dehydrogenation of alcohol being completely eliminated. The selectivity to individual amine in a mixture of amines is shown in Figure 3.14.

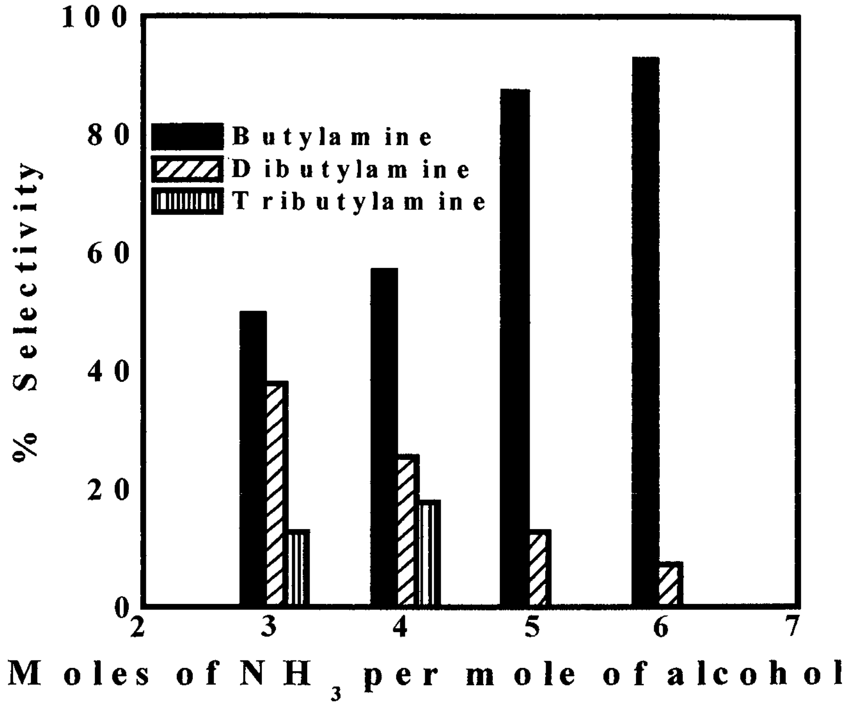

Figure 3.14 Percentage selectivity to individual amines in a mixture of amines at different alcohol to NH_3 molar ratios over 20%HPWA/HZSM-5(225) catalyst.

Weight of catalyst = 5 g	Temperature = 400 °C
LHSV = 1.00 h^{-1}	TOS = 1 h

It was observed that at a molar ratio of 1 : 5, ~ 87 % selectivity to primary amine i.e. n-butylamine was obtained and there was no formation of tertiary amine. The higher selectivity towards the primary amine at higher ammonia concentrations is attributed to the suppression of consecutive reactions that lead to dialkylated products [137].

Thus 20%HPWA/HZSM-5(225) was found to be an efficient catalyst for the ammonolysis reaction of n-butyl alcohol having a very high selectivity towards n-butylamine. Time on stream studies were carried out over 20%HPWA/HZSM-5(225) catalyst at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 5. The data is presented in Figure 3.15 and the selectivity towards individual amines in a total yield of amines at different TOS is shown in Figure 3.16.

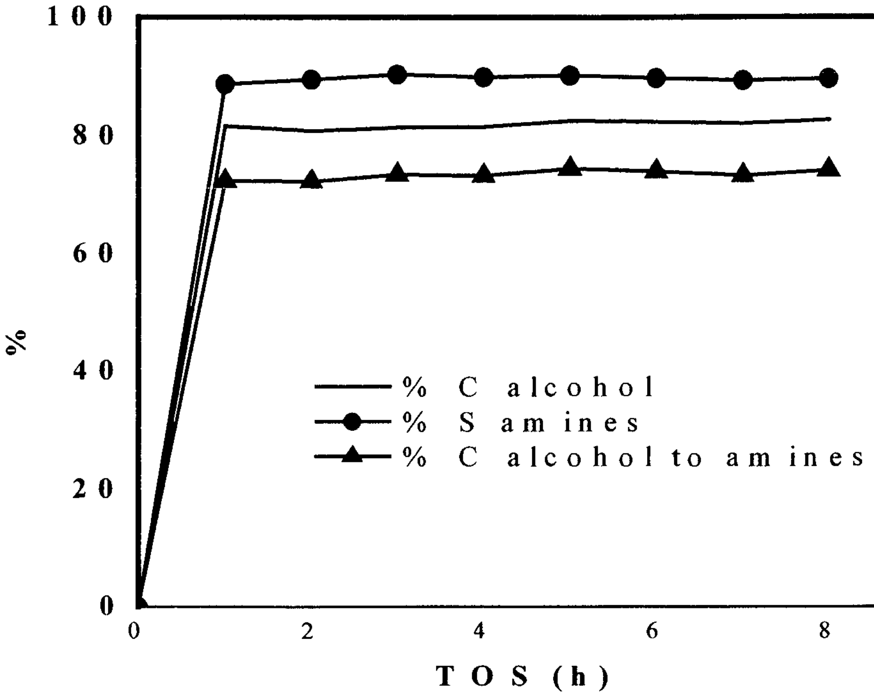

Figure 3.15 Time on stream studies over 20%HPWA/HZSM-5(225) catalyst.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 5.

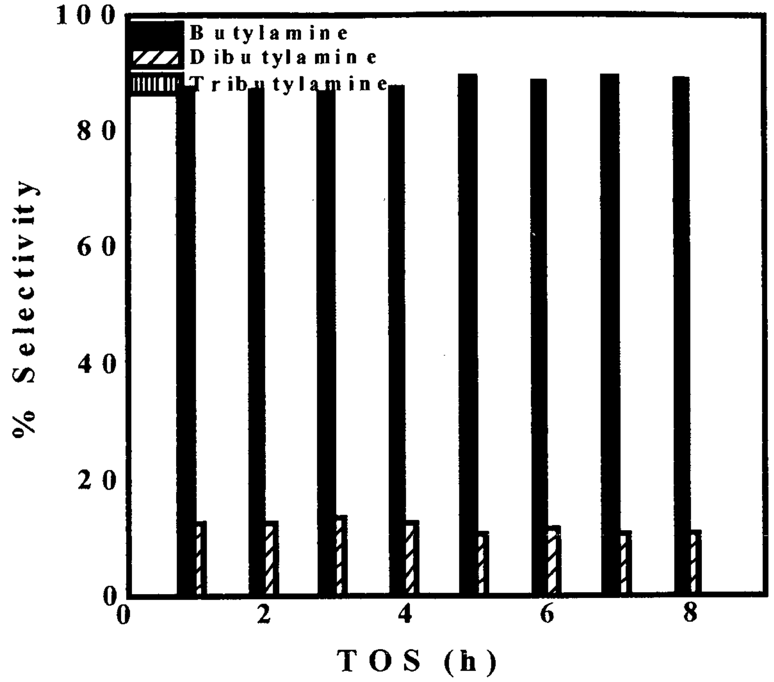

Figure 3.16 Percentage of individual amines in total amount of amines over 20%HPWA/HZSM-5(225) catalyst at different TOS.

Weight of catalyst = 5 g	Temperature = 400 °C
LHSV = 1.00 h^{-1}	Molar ratio (alcohol:NH_3) = 1 : 5

It is seen that the activity is maintained over a period of 8 hours. ~ 74 % conversion of alcohol to n-butylamine and dibutylamine is obtained with ~ 89 % selectivity to n-butylamine as seen from Figure 3.8. In addition, there is no formation of liquid by - products i.e. butyraldehyde and butyronitrile. Thus the catalyst formulation 20%HPWA/HZSM-5(225) is a successful catalyst for the synthesis of n-butylamine by direct ammonolysis of n-butyl alcohol with ammonia.

3.7 Correlation of catalytic activity with acidity of catalysts

A comparison of the active catalysts with respect to catalytic activity and selectivity under their highest yield conditions is shown in Table 3.19.

Table 3.20 Comparison of catalytic activity, selectivity and acidity of the various catalysts.

Catalyst	% C	% S 1-butene	% S amines	% C alcohol to amines	Total acidity (mmol / g)	% Acidity beyond 240 °C
HZSM-5(40)	66.58	48.77	43.44	28.92	0.47371	19.43
HZSM-5(225)	58.49	10.46	86.56	50.63	0.06964	52.39
Naβ	66.08	30.82	69.18	45.71	0.13387	49.42
HPWA	68.18	43.05	54.43	37.11	0.50115	41.27
20%HPWA/ HZSM-(225)	81.54	11.38	88.62	72.26	0.21367	60.16

A comparison of the HZSM-5(225) and 20%HPWA/HZSM-5(225) shows that for the composite catalyst the conversion of alcohol has increased by over 20 %. However the selectivity to 1-butene is almost the same. The total acidity data suggests that catalysts with very high total acidity like HZSM-5(40) or HPWA are very active for overall high conversions of the alcohol. However, a high percentage of the alcohol was converted to 1-butene, and the conversion of alcohol to amines was relatively lower at ~ 28 % for HZSM-5(40) and ~ 37 % for HPWA. On the other hand, the catalysts HZSM-5(225) and 20%HPWA/HZSM-5(225) with low total acidity showed very high conversion of alcohol to amines ~ 50 % and ~ 72 % respectively. On closer examination it was observed that these catalysts had a significantly higher concentration of acid sites beyond 240 °C. Figure 3.17 shows a correlation between percentage conversion of alcohol to amines and relative concentration of strong acid sites.

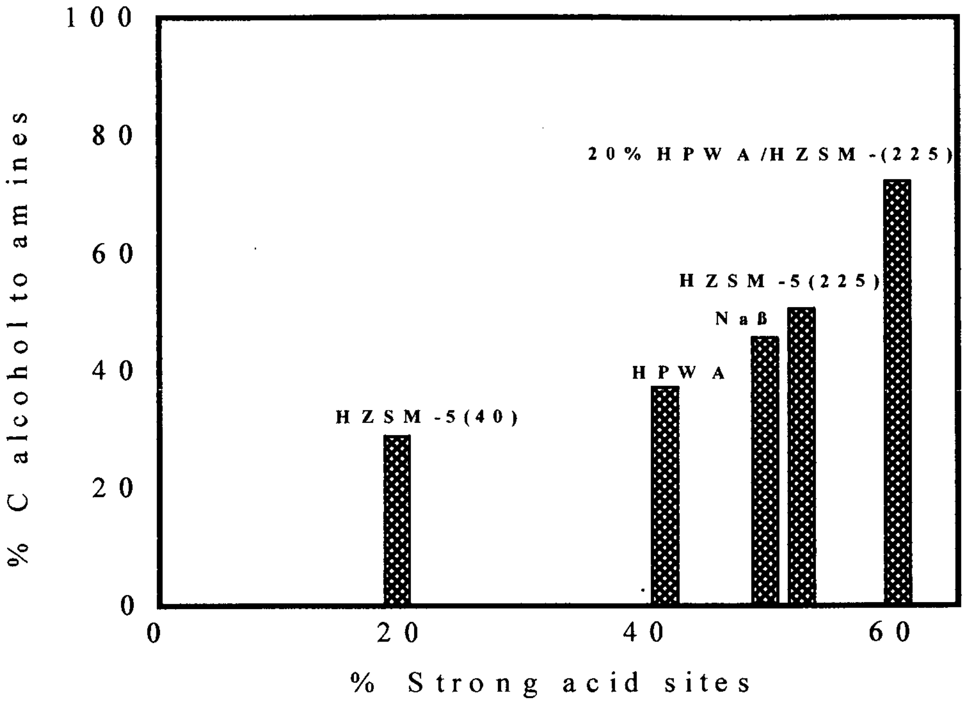

Figure 3.17 Correlation between percentage conversion of alcohol to amines and percentage of strong acid sites.

It is seen that the percentage conversion of alcohol to amines increases with a corresponding increase in relative concentration of strong acid sites for the different catalysts. Thus it is concluded that a higher proportion of relatively strong acid sites in a catalyst favours a high conversion of alcohol to amines as well as high selectivity to amines.

3.8 Conclusions

1. ZSM-5, Y, β zeolites and phosphotungstic acid are investigated as catalysts for the ammonolysis of n-butyl alcohol. The amine products were n-butylamine, dibutylamine and tributylamine.
2. It is observed that the variation of Si/Al ratio of HZSM-5 zeolite has a pronounced effect on the catalytic activity. For the three different HZSM-5 zeolite viz. HZSM-5(40), HZSM-5(80) and HZSM-5(225), it is observed that the percentage conversion of alcohol decreases as the Si/Al ratio increases. However, the selectivity towards amines and the molar percentage conversion of alcohol to amines increases with an increase in Si/Al ratio.
3. Ammonolysis occurs through Eley – Rideal type mechanism wherein the ammonia from gas phase could collide with the adsorbed alcohol to yield the butylamines.
4. TPD of ammonia is useful in elucidating reaction mechanism of ammonolysis reaction.
5. Y zeolites showed a very low activity for the formation of amines.
6. Among the β zeolites, Hβ, Cuβ, Niβ and Znβ, which gave a high dehydration activity, showed a poor activity towards formation of amines. The dehydration activity of Naβ was relatively less. The decrease in dehydration activity was associated with enhanced formation of amines.
7. Naβ zeolite was found to be highly active catalyst for the selective synthesis of dibutylamine. Highest conversion of alcohol to amines at high selectivity towards dibutylamine (~ 55 %) was observed at a temperature of 450 °C,

LHSV of 0.75 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 3 over Naβ zeolite catalyst. Under the same conditions of temperature and LHSV but at an alcohol to NH_3 molar ratio of 1 : 6, the selectivity to n-butylamine was ~ 54 %.

8. HZSM-5(225) zeolite was found to be the most active catalyst for the synthesis of amines by the reaction of n-butyl alcohol and ammonia among all the zeolite catalysts showing ~ 50 % conversion of alcohol to amines at a temperature of 400 °C, LHSV of 1.25 h^{-1} and alcohol to ammonia molar ratio of 1 : 5.
9. Catalysts having very high acidity such as HPWA and HZSM-5(40) which gave a high dehydration activity, exhibited a poor selectivity towards formation of amines.
10. The catalyst 20%HPWA/HZSM-5(225) was found to be the most active catalyst and showed a high selectivity towards n-butylamine. Highest conversion of alcohol to amines (~ 73 %) was observed at a temperature of 400 °C, LHSV of 1.00 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 5.
11. Relatively strong acid sites favour a high conversion of alcohol to amines as well as high selectivity to amines.

Chapter 4

Ammonolysis of sec-butyl alcohol

Ammonolysis of sec-butyl alcohol

This Chapter describes the catalytic activity of various catalysts for the synthesis of sec-butylamines by the ammonolysis reaction of sec-butyl alcohol with ammonia. The ammonolysis reaction of sec-butyl alcohol is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia over ZSM-5, Y and β zeolites and phosphotungstic acid. 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 formation of undesirable products. The catalytic activity is correlated to the catalyst characteristics.

4.1 Reaction Procedure

The ammonolysis of sec-butyl alcohol was carried out in a vertical flow type of a reactor system similar to the one used for the ammonolysis of n-butyl alcohol. In a typical experiment 5 g of the catalyst is packed in a quartz reactor. The catalyst is activated in flowing air for about 6 hours at 500 °C. The temperature is then brought to the reaction temperature in dry nitrogen. Sec-butyl alcohol (E - Merck, commercial, distilled) and anhydrous ammonia (99.8 %, Bhoruka Gases Pvt. Ltd.) are then passed through the reactor, from a Miclins syringe peristaltic 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 sec-butyl alcohol i.e. liquid hourly space velocity (LHSV). The reactants are mixed in a preheater cum mixer and then passed over the catalysts. The products are then analysed by online gas chromatography with a chemito 8610 HT gas chromatograph using carbowax 20 M KOH treated column and 5 % SE - 30 column. The products of the reaction were found to be the three amines i.e. sec-butylamine (sBA), di-sec-butylamine (sDBA) and tri-sec-butylamine (sTBA), ethyl methyl ketone and 2-butene.

The calculations for molar percentage conversion, molar percentage selectivity to products and total selectivity to amines, percentage molar conversion of alcohol to amines and percentage selectivity to individual amines in a mixture of amines are similar to that as shown for the ammonolysis reaction of n-butyl alcohol.

4.2 Ammonolysis of sec-butyl alcohol over ZSM-5 zeolite catalysts

HZSM-5(40) was taken as a model catalyst to optimise the conditions for the comparison of catalytic activity of various catalysts. The effect of temperature on ammonolysis reaction of sec-butyl alcohol at a LHSV of 1.00 h^{-1} and a molar ratio of alcohol: ammonia of 1 : 4 over HZSM-5(40) is shown in Table 4.1.

Table 4.1 Effect of temperature on ammonolysis reaction of sec-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
250	17.39	68.17	2.77	17.52	6.13	5.41	29.06	5.05
300	24.68	62.16	2.76	18.64	9.12	7.32	35.08	8.66
350	32.61	59.51	1.53	20.32	12.51	6.13	38.96	12.70
400	**49.74**	**49.54**	**2.39**	**31.16**	**9.62**	**7.29**	**48.07**	**23.91**
450	54.92	72.04	--	16.10	7.32	4.54	27.96	15.36

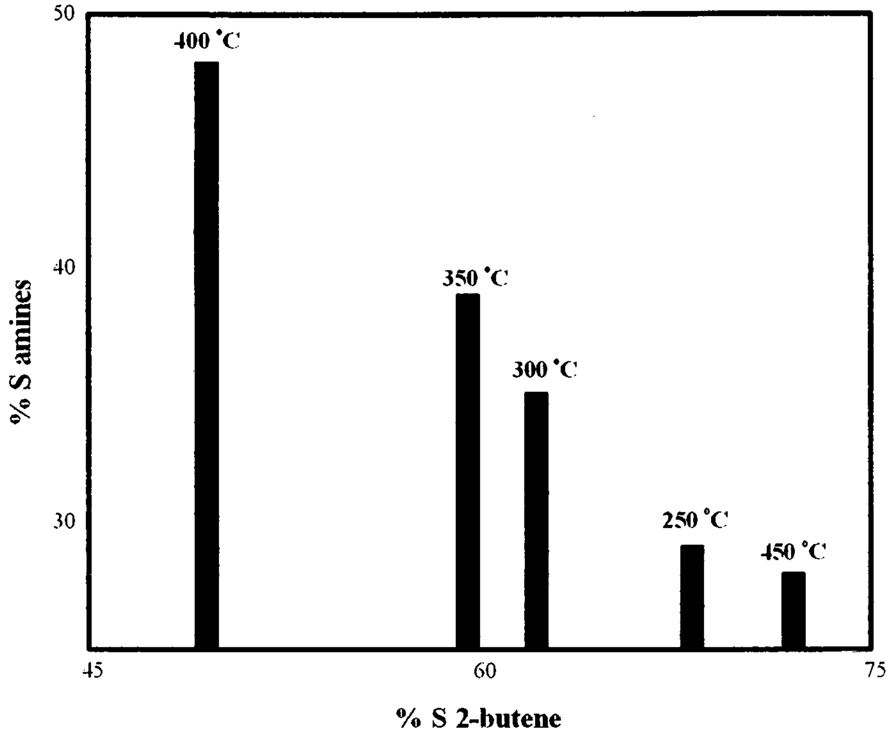

Figure 4.1 Correlation between selectivity to amines and selectivity to 2-butene amines at various temperatures.

Weight of catalyst = 5 g	LHSV = 1.00 h^{-1}
Molar Ratio (alcohol : NH_3) = 1 : 4	TOS = 1 h

Figure 4.1 shows the correlation between selectivity to amines and selectivity to 2-butene at various temperatures. It is observed that very low conversions of alcohol occurred at lower temperatures. The conversion of alcohol increased with increase in temperature. Similarly the selectivity towards amines also increased but only upto 400 °C. This increased selectivity was associated with decreased conversion to 2-butene. At 450 °C, when the conversion to 2-butene became more, amine

formation also decreased. Thus ammmnolysis reaction does not seem to occur through addition of ammonia to 2-butene.

The reaction was further studied for LHSV variations at a temperature of 400 °C and an alcohol to ammonia molar ratio of 1 : 4. The data is presented in Table 4.2.

Table 4.2. Effect of LHSV on ammonolysis reaction of sec-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
0.50	56.07	64.06	--	18.31	10.54	7.09	35.94	20.15
1.00	49.74	49.54	2.39	31.16	9.62	7.29	48.07	23.91
1.50	**48.90**	**33.06**	**2.32**	**38.34**	**14.61**	**11.67**	**64.62**	**31.60**
2.00	39.47	53.18	--	25.99	12.49	8.34	46.82	18.48

It was observed that the percentage conversion increased with a decrease in LHSV, i. e. increase in contact time of the alcohol with the catalyst. The highest selectivity to amine (~ 65 %) was obtained at a LHSV of 1.50 h^{-1}.

The effect of molar ratio on the ammonolysis reaction of sec-butyl alcohol over HZSM-5(40) is shown in Table 4.3.

Table 4.3 Effect of molar ratio on ammonolysis reaction of sec-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.50 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
1 : 3	49.15	51.56	--	28.25	13.17	7.02	48.44	23.80
1 : 4	**48.90**	**33.06**	**2.32**	**38.34**	**14.61**	**11.67**	**64.62**	**31.60**
1 : 5	46.13	36.27	2.95	40.11	12.19	8.48	60.78	28.03
1 : 6	48.58	50.11	--	38.17	9.02	2.70	49.89	24.23

Thus the best yields on HZSM-5(40) were obtained at a temperature of 400 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4. The catalytic activity of various ZSM-5 zeolite catalysts was evaluated under these conditions. The results are presented in Table 4.4.

Table 4.4 Catalytic activity of various ZSM-5 zeolite catalysts for the ammonolysis reaction of sec-butyl alcohol.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.50 h^{-1}

TOS = 1h

Molar Ratio (alcohol : NH_3) = 1 : 4

Catalyst	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
HZSM-5(40)	**48.90**	**33.06**	**2.32**	**38.34**	**14.61**	**11.67**	**64.62**	**31.60**
HZSM-5(80)	42.74	42.82	2.26	30.61	13.29	11.02	54.92	23.47
HZSM-5(225)	39.36	53.48	--	29.66	10.69	6.17	46.52	18.31
NaZSM-5	26.31	65.33	--	19.65	8.68	6.34	34.67	9.12
CuZSM-5	47.21	58.42	--	29.07	12.51	--	41.58	19.63
NiZSM-5	45.09	56.03	--	19.62	13.61	10.74	43.97	19.83
ZnZSM-5	19.60	68.38	2.30	14.84	9.32	5.16	29.32	5.75

It was observed that for the HZSM-5 zeolite catalysts of different Si/Al ratios (viz. 40, 80 and 225) the percentage conversion of alcohol and percentage selectivity to amines and molar percentage conversion of alcohol to amines decreased as Si/Al ratio increased. The total acidity for the three HZSM-5 zeolites also decreased as Si/Al ratio increased. Thus it is found that the variation of Si/Al ratio of HZSM-5 zeolite has a pronounced effect on the catalytic activity. A comparison of catalytic activity and acidity – basicity data of various ZSM-5 zeolite catalysts is shown in Table 4.5.

Table 4.5 Comparison of catalytic activity, total acidity and total basicity of various ZSM-5 zeolite catalysts.

Catalyst	% C alcohol	%S 2-Butene	% S amines	% C alcohol to amines	Total acidity (mmol / g)	Total basicity (μmol / g)
HZSM-5(40)	48.90	33.06	64.62	31.60	0.47371	0.01547
HZSM-5(80)	42.74	42.82	54.92	23.47	0.23446	0.02850
HZSM-5(225)	39.36	53.48	46.52	18.31	0.06964	0.04189
NaZSM-5	26.31	65.33	34.67	9.12	0.03674	0.06842
CuZSM-5	47.21	58.42	41.58	19.63	0.09757	0.01662
NiZSM-5	45.09	56.03	43.97	19.83	0.13024	0.02374
ZnZSM-5	19.60	68.38	29.32	5.75	0.06924	0.02482

It was observed that the ZSM-5 zeolites with lower acidities were less active compared to the highly acidic ZSM-5 zeolite i.e. HZSM-5(40). It can be seen from Table 4.5 that the ZSM-5 zeolite catalyst with highest total acidity and lowest total basicity is the most active catalyst i. e. HZSM-5(40). Catalysts with low total acidity and a high total basicity such as NaZSM-5 and ZnZSM-5 exhibited a poor catalytic activity for the ammonolysis reaction. Ion exchanged zeolites NiZSM-5 and CuZSM-5 with higher total acidity and lower total basicity were more active than NaZSM-5 zeolite. Thus a high total acidity and a low total basicity favoured the formation of sec-butylamines by the reaction of n-butyl alcohol and ammonia over ZSM-5 zeolites.

Thus HZSM-5 (40) was found to be the most active catalyst among various ZSM-5 zeolites showing ~ 31 % conversion of alcohol to amines at a temperature of 400 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4.

4.3 Ammonolysis of sec-butyl alcohol over Y zeolite catalysts

The catalytic activity of various Y zeolite catalysts was determined at the preoptimised temperature of 400 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4. The results are presented in Table 4.6.

Table 4.6 Catalytic activity of various Y zeolite catalysts for the ammonolysis reaction of sec-butyl alcohol.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.50 h^{-1}

TOS = 1h

Molar Ratio (alcohol : NH_3) = 1 : 4

Catalyst	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
NaY	30.34	46.64	--	27.32	12.44	13.60	53.36	16.19
HY	**59.85**	**26.82**	**3.82**	**41.07**	**17.19**	**11.10**	**69.36**	**41.51**
CuY	41.56	50.09	1.96	24.32	13.42	10.21	47.95	19.93
NiY	38.24	48.63	--	34.41	16.96	--	51.37	19.64
ZnY	34.17	50.19	1.47	24.47	13.95	9.92	48.34	16.52

It is observed from Table 4.6 that the protonic zeolite HY shows a high activity for the conversion of alcohol (~ 60 %). The selectivity to amines is also very high (~ 70 %). Thus HY zeolite is found to be the most active catalyst from the different Y zeolite catalysts screened. The other Y zeolite catalysts show a lower activity for the conversion of alcohol. Also the dehydration activity is very high over these catalysts (~ 50 %) thereby reducing the selectivity towards amines. In comparison, the dehydration activity of the protonic form HY was much lower (~ 26 %). This was accompanied by a high selectivity towards amines (~ 60 %). The catalytic activity for Y zeolites follows the order NaY < ZnY < NiY < CuY < HY. A comparison of catalytic activity and acidity - basicity data of various Y zeolite catalysts is shown in Table 4.7.

Table 4.7 Comparison of catalytic activity, total acidity and total basicity of various Y zeolite catalysts.

Catalyst	% C alcohol	%S 2-Butene	% S amines	% C alcohol to amines	Total acidity (mmol / g)	Total basicity (μmol / g)
NaY	30.34	46.64	53.36	16.19	0.09837	0.06864
HY	59.85	26.82	69.36	41.51	0.38525	0.01545
CuY	41.56	50.09	47.95	19.93	0.21290	0.03034
NiY	38.24	48.63	51.37	19.64	0.19767	0.03582
ZnY	34.17	50.19	48.34	16.52	0.11478	0.04201

It can be seen from Table 4.7 that Y zeolite catalyst possessing highest total acidity and lowest total basicity i. e. HY zeolite is the most active catalyst. The catalytic activity for the remaining Y zeolites also follows the same pattern i. e. conversion of alcohol to amines increases with increase in total acidity of the Y zeolite catalysts and decreases with increase in total basicity indicating that acidity and basicity play a crucial role in the controlling the yield of amines. Acid base pairs have been shown to be active sites for the amination of methanol [61 - 67]. A similar kind of system may be operative over here also. Thus it can be concluded that a high total acidity and a low total basicity favours the formation of sec-butylamines by the reaction of sec-butyl alcohol and ammonia over Y zeolites.

HY zeolite showed higher a catalytic activity than HZSM-5(40) zeolite. Hence the reaction was further investigated for temperature, LHSV and alcohol to ammonia molar ratio variations over this catalyst in order to optimize conditions to obtain the best yields of amines on these catalysts. Table 4.8 shows the effect of temperature on the ammonolysis reaction of sec-butyl alcohol over HY zeolite at a LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4.

Table 4.8 Effect of temperature on ammonolysis reaction of sec-butyl alcohol over HY zeolite.

Weight of catalyst = 5 g

LHSV = 1.50 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
350	44.32	43.37	1.74	30.52	14.34	10.03	54.89	24.33
400	**59.85**	**26.82**	**3.82**	**41.07**	**17.19**	**11.10**	**69.36**	**41.51**
450	64.76	62.76	--	18.16	10.12	8.96	37.24	24.12

The percentage conversion of alcohol increased with increase in temperature. However the highest conversion of alcohol to amines is obtained at a temperature of 400 °C owing to a high selectivity towards amines.

The effect of LHSV on the ammonolysis reaction over HY zeolite is shown in Table 4.9.

Table 4.9 Effect of LHSV on ammonolysis reaction of sec-butyl alcohol over HY zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
0.50	69.82	34.83	--	32.01	14.44	18.72	65.17	45.50
1.00	**66.95**	**18.58**	**3.59**	**48.08**	**21.29**	**13.51**	**82.88**	**55.48**
1.50	59.85	26.82	3.82	41.07	17.19	11.10	69.36	41.51
2.00	52.16	41.55	--	33.58	14.18	10.69	58.45	30.49

The percentage conversion of alcohol increases as LHSV is decreased however the highest molar percentage conversion of alcohol to amines is obtained at a LHSV of 1.00 h^{-1} (~ 55 %). A wide variation is observed in the selectivity towards amines at different LHSVs, which indicates that the contact time plays a crucial role in controlling the selectivity towards amines apart from affecting the selectivity towards a particular amine. At LHSV of 0.50 h^{-1}, a high selectivity was observed towards 2-butene, which resulted in an overall low yield of amines.

The effect of alcohol to ammonia molar ratio on the ammonolysis reaction over HY zeolite is shown in Table 4.10.

Table 4.10 Effect of molar ratio on ammonolysis reaction of sec-butyl alcohol over HY zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
1 : 2	73.18	31.01	--	24.74	34.12	10.13	68.99	50.49
1 : 3	71.54	20.60	3.67	29.48	30.17	16.08	75.73	54.18
1 : 4	66.95	18.58	3.59	48.08	21.29	13.51	82.88	55.48
1 : 5	**68.81**	**14.33**	--	**66.19**	**12.10**	**7.38**	**85.67**	**58.95**
1 : 6	66.17	22.67	--	64.92	9.03	3.38	77.33	51.17

It is observed from Table 4.10 that the highest selectivity towards amines (~ 85 %) is obtained at an alcohol to ammonia molar ratio of 1:5. The conversion of alcohol was also highest under this condition. The relative proportion of an individual amine in a total yield of amines is shown in Figure 4.2.

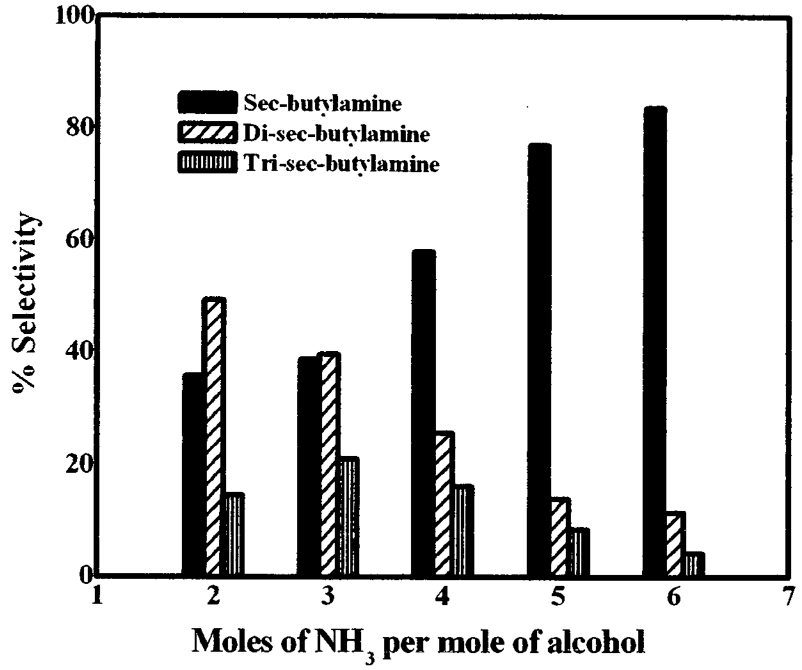

Figure 4.2 Selectivity towards an individual amine in a mixture of amines over HY zeolite at different alcohol to ammonia ratios.

Weight of catalyst = 5 g	Temperature = 400 °C
LHSV = 1.00 h^{-1}	TOS = 1 h

It can be seen from Figure 4.2 that the molar ratio affects the selectivity towards an individual amine significantly. Thus the selectivity towards the sec-butylamine rises from ~ 35 % at an alcohol to ammonia molar ratio of 1 : 2 to ~ 85 % at an alcohol to ammonia molar ratio of 1 : 6 with a corresponding decrease in selectivity towards secondary and tertiary amines. This trend of higher selectivity towards the primary amine at higher ammonia concentrations is attributed to the suppression of consecutive reactions that lead to dialkylated products and is previously reported [137]. Thus the best yields of amines over HY zeolite were obtained at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of of 1 : 5 where in ~ 59 % of the alcohol is converted into amines at a high selectivity towards sec-butylamine.

The time on stream studies were carried out on HY zeolite at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of of 1 : 5 to study the catalytic activity variations with time. The results are shown in Figure 4.3.

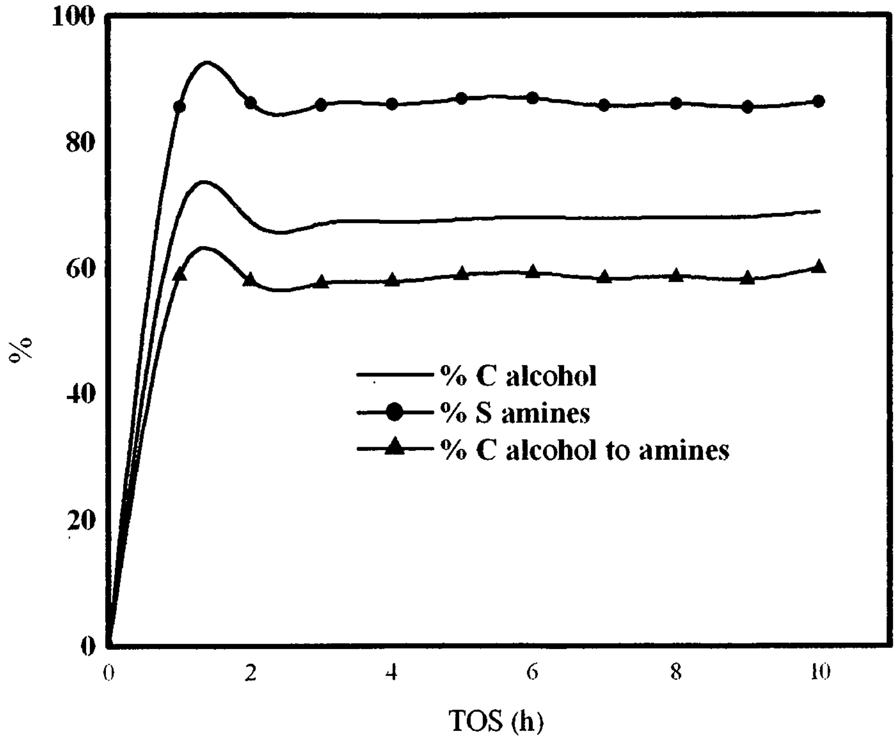

Figure 4.3 Time on stream studies for the ammonolysis reaction of sec-butyl alcohol over HY zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 5

The catalyst showed a nearly constant activity for the formation of amines over a period of 10 hours, and also no formation of ethyl methyl ketone was observed over this period. However, the selectivity towards sec-butylamine dropped considerably by the tenth hour, with a corresponding increase in selectivity towards tri-sec-butylamine by ~ 4 % (not shown in Figure). Thus although the HY zeolite catalyst showed a higher catalytic activity for the ammonolysis reaction compared to HZSM-5(40) zeolite, formation of all three amines and a decrease in selectivity towards the primary amine over a period of time, were the drawbacks observed over this catalyst.

4.4 Ammonolysis of sec-butyl alcohol over β zeolite catalysts

The catalytic activity of various β zeolite catalysts was determined at the preoptimised temperature of 400 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4. The results are presented in Table 4.11.

Table 4.11 Catalytic activity of various β zeolite catalysts for the ammonolysis reaction of sec-butyl alcohol.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.50 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1h

Catalyst	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
Naβ	31.84	60.43	--	20.64	12.13	6.80	39.57	12.60
Hβ	**62.09**	**49.06**	**--**	**28.51**	**13.98**	**8.45**	**50.94**	**31.63**
Cuβ	41.52	61.90	--	22.82	15.28	--	38.10	15.82
Niβ	33.97	62.38	--	26.11	8.97	2.54	37.62	12.78
Znβ	40.73	57.34	1.98	25.53	15.35	--	40.68	16.57

It is observed from Table 4.11 that the protonic zeolite Hβ shows a high activity for conversion of the alcohol (~ 62 %). The selectivity to amines is also high (~ 50 %). Thus Hβ zeolite is found to be the most active catalyst from the different β zeolite catalysts screened. The other β zeolite catalysts show a lower activity for the conversion of alcohol (~ 30 – 40 %). Also the dehydration activity is very high over these catalysts (~ 60 %) thereby reducing the selectivity towards amines. The catalytic activity for the various β zeolites followed the order Naβ < Niβ < Cuβ < Znβ < Hβ. A comparison of catalytic activity and acidity - basicity data of various β zeolite catalysts is shown in Table 4.12.

Table 4.12 Comparison of catalytic activity, total acidity and total basicity of various β zeolite catalysts.

Catalyst	% C alcohol	%S 2-Butene	% S amines	% C alcohol to amines	Total acidity (mmol / g)	Total basicity (μmol / g)
Naβ	31.84	60.43	39.57	12.60	0.13387	0.05218
Hβ	62.09	49.06	50.94	31.63	0.48694	0.01634
Cuβ	41.52	61.90	38.10	15.82	0.17840	0.03564
Niβ	33.97	62.38	37.62	12.78	0.16653	0.03887
Znβ	40.73	57.34	40.68	16.57	0.19475	0.03317

It can also be seen from Table 4.12 that β zeolite catalyst possessing highest total acidity and lowest total basicity i. e. Hβ zeolite is the most active catalyst. The catalytic activity for the remaining β zeolites also follows the same pattern i. e. conversion of alcohol to amines increases with increase in total acidity of the β zeolite catalysts and decreases with increase in total basicity. Thus it is observed that the catalysts having a high total acidity and a low total basicity have a higher activity for the formation of sec-butylamines by the reaction of sec-butyl alcohol and ammonia over β zeolites. Thus it can be concluded that a high total acidity and a low total basicity favours the formation of sec-butylamines by the reaction of sec-butyl alcohol and ammonia over β zeolites.

Hβ zeolite showed a catalytic activity comparable to HZSM-5(40) zeolite. Hence the reaction was further investigated for temperature, LHSV and alcohol to ammonia molar ratio variations over Hβ zeolite in order to optimize the conditions for obtaining the best yield of amines as well as to get more insight into the reaction.

The effect of temperature on the ammonolysis reaction of sec-butyl alcohol over Hβ zeolite at a LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4 is shown in Table 4.13.

Table 4.13 Effect of temperature on ammonolysis reaction of sec-butyl alcohol over Hβ zeolite.

Weight of catalyst = 5 g

LHSV = 1.50 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
350	51.73	50.14	1.58	23.17	14.51	10.60	48.28	24.98
400	**62.09**	**49.06**	--	**28.51**	**13.98**	**8.45**	**50.94**	**31.63**
450	72.13	60.29	--	25.37	10.38	3.96	39.71	28.64

The highest conversion of alcohol to amines is obtained at a temperature of 400 °C. The catalyst showed a predominant selectivity towards sec-butylamine at all three temperatures.

The effect of LHSV on the ammonolysis reaction over Hβ zeolite is shown in Table 4.14.

Table 4.14 Effect of LHSV on ammonolysis reaction of sec-butyl alcohol over Hβ zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
0.50	67.82	56.67	1.64	15.98	13.16	12.55	41.69	28.27
1.00	65.75	53.58	--	22.38	12.44	11.60	46.42	30.52
1.50	62.09	49.06	--	28.51	13.98	8.45	50.94	31.63
2.00	**60.32**	**27.46**	--	**50.16**	**18.78**	**3.60**	**72.54**	**43.75**
2.50	54.17	31.87	--	50.11	15.01	3.01	68.13	36.90

Higher conversions of alcohol are obtained at lower LHSVs i. e. 0.50 h^{-1}, 1.00 h^{-1} and 1.50 h^{-1}. However, the yield of amines is lowered under these conditions due to a high selectivity towards 2-butene. It is seen that the highest conversion of alcohol to amines is obtained at a LHSV of 2.00 h^{-1} owing to a lowered dehydration activity (~ 27 %). Also the selectivity towards the primary amine is very high under this condition. It is thus observed that with increasing LHSVs the proportion of primary amine increases. Thus when the reactants spend a shorter time on the catalyst (high LHSV), as expected the probability of further alkylation of primary amine to form secondary and tertiary amines is low. Hence there is predominant selectivity towards sec-butylamine at higher LHSVs. At lower LHSVs, the secondary and tertiary amines are formed at the expense of primary amine.

Further investigation was carried out to study the effect of molar ratio of alcohol to NH_3 on the ammonolysis reaction over Hβ zeolite at a temperature of 400 °C and a LHSV of 2.00 h^{-1}. The data is presented in Table 4.15.

Table 4.15 Effect of molar ratio on ammonolysis reaction of sec-butyl alcohol over Hβ zeolite.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 2.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
1 : 3	62.56	30.55	1.12	35.82	23.54	8.97	68.33	42.74
1 : 4	60.32	27.46	--	50.16	18.78	3.60	72.54	43.75
1 : 5	**62.13**	**20.87**	--	**64.18**	**10.65**	**4.30**	**79.13**	**49.16**
1 : 6	61.58	27.46	--	60.95	7.78	3.81	72.54	44.67

Though the conversion of alcohol at various molar feed ratios of alcohol to ammonia is almost the same, the selectivity towards amines varies significantly resulting in varying overall yields. Thus the best yields over Hβ zeolite are obtained at a temperature of 400 °C, LHSV of 2.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 5 where in ~ 62 % conversion of the alcohol occurs at ~ 80 % selectivity towards amines out of which ~ 65 % is sec-butylamine. Thus Hβ zeolite is found to be an efficient catalyst for the synthesis of sec-butylamine by the ammonolysis reaction of sec-butyl alcohol.

Time on stream studies were carried out over Hβ zeolite at a temperature of 400 °C, LHSV of 2.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 5. The results are shown in Figure 4.4.

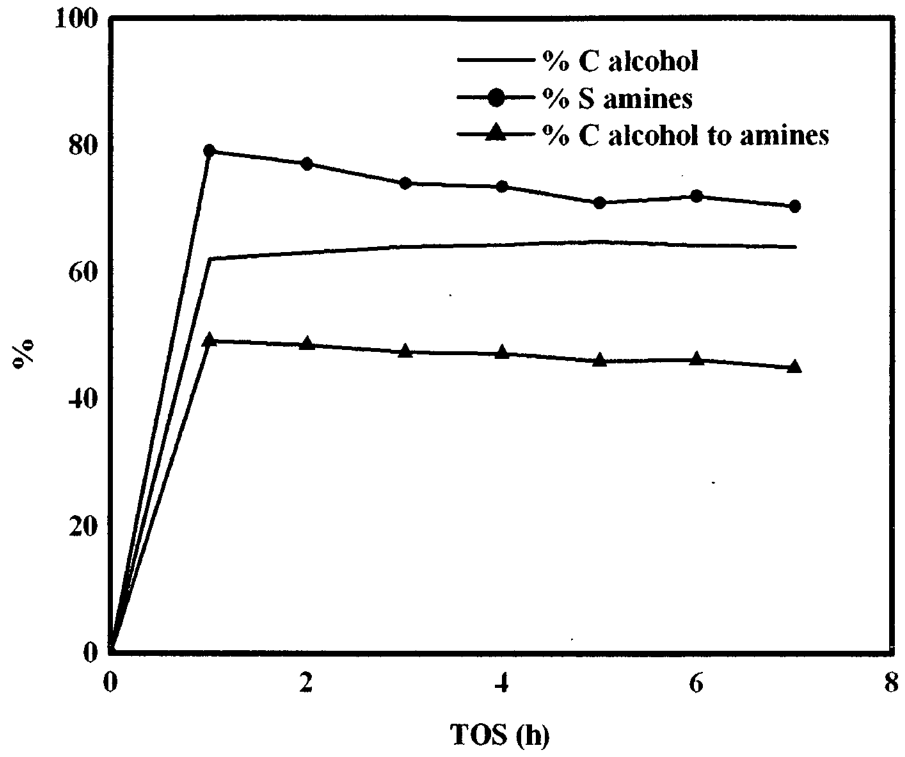

Figure 4.4 Time on stream studies for the ammonolysis reaction of sec-butyl alcohol over Hβ zeolite.

Weight of catalyst = 5 g Temperature = 400 ^{0}C

LHSV = 2.00 h^{-1} Molar Ratio (alcohol : NH_3) = 1 : 5

It can be seen from Figure 4.4 that although the conversion of alcohol increases by ~ 2 %, the conversion of alcohol to amines decreases by ~ 5 % over a 7 hour period. A possible reason for the decreased selectivity could be the coking of zeolite catalyst by the high amounts of alkene formed in the initial period.

The selectivity towards sec-butylamine also decreases by ~ 4 % by the seventh hour (not shown in Figure). Thus although Hβ zeolite shows ~ 50 % conversion of alcohol into amines, however it suffers from the drawback of a decreasing activity with time due to increased selectivity towards dehydration of sec-butyl alcohol to 2-butene and also a decreasing selectivity towards the desirable amine i.e. sec-butylamine.

Thus HY zeolite was found to be the most active zeolite catalyst for synthesis of sec-butylamines via the ammonolysis reaction of sec-butyl alcohol among the various zeolite catalysts studied. Also HZSM-5(40) and Hβ showed an appreciable activity for the ammonolysis reaction. The major problem associated with these catalysts was the dehydration of alcohol to give 2-butene and also the mixed selectivities observed towards different amines. Thus these zeolite catalysts though quite active for the reaction were found to be lacking in selectivity towards an individual amine. The above three active catalysts are highly acidic. Therefore the catalytic activity of phosphotungstic acid (HPWA) which possessed a much higher total acidity compared to the above three protonic zeolite catalysts was evaluated for the ammonolysis reaction to obtain more insight into the reaction.

4.5 Ammonolysis of sec-butyl alcohol over phosphotungstic acid (HPWA)

The reaction as before was investigated for temperature, LHSV and alcohol to ammonia molar ratio variations over HPWA in order to optimize the conditions for obtaining the best yield of amines.

The effect of temperature on ammonolysis reaction of sec-butyl alcohol over HPWA catalyst was studied at a LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4 is shown in Table 4.16.

Table 4.16 Effect of temperature on ammonolysis reaction of sec-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
300	64.17	59.83	1.08	19.17	14.02	5.90	39.09	25.08
350	**70.12**	**61.22**	**1.20**	**23.13**	**10.98**	**3.47**	**37.58**	**26.35**
400	80.89	71.08	--	22.75	6.17	--	28.92	23.39
450	86.13	82.65	--	16.13	1.22	--	17.35	14.94

Very high conversions of sec-butyl alcohol were observed over HPWA catalyst (~ 85 % at 450 °C) as in the case of n-butyl alcohol. However the selectivity towards amines was found to be low (a maximum of ~ 38 % at 350 °C) due to a high dehydration activity. The relative proportion of sec-butylamine increased with an increase in temperature as expected. The effect of LHSV on the ammonolysis reaction of sec-butyl alcohol over HPWA catalyst is shown in Table 4.17.

Table 4.17 Effect of LHSV on ammonolysis reaction of sec-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

Temperature = 350 °C

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
0.50	74.13	66.73	2.95	6.92	10.56	2.84	30.32	22.47
1.00	70.12	61.22	1.20	23.13	10.98	3.47	37.58	26.35
1.50	66.94	63.10	--	23.12	8.98	4.80	36.90	24.70
2.00	**64.42**	**54.13**	--	**33.02**	**9.28**	**3.57**	**45.87**	**29.54**
2.50	58.73	64.46	--	26.42	9.12	--	35.54	20.87

It is observed that although very high conversions are obtained over HPWA, a high selectivity towards 2-butene lowers the selectivity towards amines. The highest conversion of alcohol to amines is obtained at a LHSV of 2.00 h^{-1}. At lower LHSVs, the selectivity towards the primary amine is lowered and selectivity towards the secondary and tertiary amines is increased as observed in the case of zeolites.

The reaction was further investigated to study the effect of alcohol to ammonia molar ratio on the ammonolysis reaction of sec-butyl alcohol over HPWA catalyst. The data is shown in Table 4.18.

Table 4.18 Effect of molar ratio on ammonolysis reaction of sec-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

Temperature = 350 °C

LHSV = 2.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
1 : 3	66.13	61.58	--	24.13	9.02	5.27	38.42	25.40
1 : 4	64.42	54.13	--	33.02	9.28	3.57	45.87	29.54
1 : 5	**65.07**	**51.12**	--	**40.93**	**7.95**	--	**48.88**	**31.80**
1 : 6	62.18	64.78	--	31.73	3.54	--	35.27	21.93

The best yields of amines (~ 31 %) over HPWA catalyst was obtained at a temperature of 350 °C, LHSV of 2.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 5. Under this condition the catalyst showed a high selectivity towards the formation of sec-butylamine.

Thus HPWA catalyst showed a lower activity for the ammonolysis of sec-butyl alcohol compared to HY and Hβ zeolite catalysts but the activity was comparable to that of HZSM-5(40) zeolite. However the catalyst showed very high overall conversions of sec-butyl alcohol and also a high selectivity towards sec-butylamine at higher ammonia to alcohol ratios.

4.6 Ammonolysis of sec-butyl alcohol over HPWA/HY composite catalysts

Mixtures of HPWA with the most active zeolite i. e. HY zeolite were prepared to investigate:

(i) yields of amines

(ii) effect of catalyst modification on catalytic activity and

(iii) to elucidate the active sites for the ammonolysis reaction.

A series of catalyst formulations of different compositions ranging from 10% HPWA to 40% HPWA were made in combination with HY zeolite. The resultant composite catalysts showed variable acidity patterns as compared to the individual catalysts as can be seen from Figure 2.23. An interesting result was the total acidity of composite catalysts 10%HPWA/HY and 20%HPWA/HY, which showed lower total acidities as compared to both the individual catalysts i.e. HPWA and HY, indicating some kind of structural interaction between the components.

The catalyst formulation 20%HPWA/HY was taken as the model catalyst to optimise the conditions to evaluate the catalytic activity of the other composite catalysts.

The reaction was investigated over 20%HPWA/HY as a function of temperature, LHSV and molar ratio variations.

The effect of temperature on the ammonolysis reaction of sec-butyl alcohol over 20%HPWA/HY catalyst was evaluated at a LHSV of 1.00h^{-1} and an alcohol to ammonia molar ratio of 1 : 4. The data is shown in Table 4.19.

Table 4.19 Effect of temperature on ammonolysis reaction of sec-butyl alcohol over 20%HPWA/HY catalyst.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
350	69.84	25.88	--	41.17	18.94	14.01	74.12	51.76
400	**78.08**	**13.13**	**--**	**57.98**	**19.12**	**9.77**	**86.87**	**67.82**
450	84.35	34.16	--	52.16	10.82	2.86	65.84	55.53

The conversions obtained over 20%HPWA/HY catalyst were higher compared to pure HY zeolite (~ 85 % at 450 °C). ~ 68 % conversion of alcohol to amines takes place at a temperature of 400 °C. The selectivity towards 2-butene is also low (~ 12 %) at this temperature. Also mixed selectivities were observed for amines at all temperatures.

Table 4.20 shows the effect of LHSV on ammonolysis reaction of sec-butyl alcohol over 20%HPWA/HY catalyst.

Table 4.20 Effect of LHSV on ammonolysis reaction of sec-butyl alcohol over 20%HPWA/HY catalyst.

Weight of catalyst = 5 g

Temperature = 400 °C

Molar Ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
0.50	82.36	36.40	--	39.58	13.31	10.71	63.60	52.38
1.00	**78.08**	**13.13**	--	**57.98**	**19.12**	**9.77**	**86.87**	**67.82**
1.50	71.45	19.54	--	52.98	17.71	9.77	80.46	57.48
2.00	68.27	20.83	--	51.74	18.95	8.48	79.17	51.32

The highest yields are obtained at a LHSV of 1.00h^{-1} where in ~ 68 % of sec-butyl alcohol is converted to amines. The effect of alcohol to ammonia molar ratio variations on the ammonolysis reaction is shown in the Table 4.21 and the percentage selectivity towards the individual amine in a total yield of amines over 20%HPWA/HY catalyst at different alcohol to ammonia molar ratios is shown in Figure 4.5.

Table 4.21 Effect of molar ratio on ammonolysis reaction of sec-butyl alcohol over 20%HPWA/HY catalyst.

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
1 : 3	80.49	26.52	2.12	42.26	18.78	10.32	71.36	57.43
1 : 4	78.08	13.13	--	57.98	19.12	9.77	86.87	67.82
1 : 5	79.42	16.02	--	62.26	16.77	4.95	83.98	66.69
1 : 6	**76.43**	**8.76**	--	**80.55**	**10.69**	--	**91.24**	**69.73**
1 : 7	75.93	12.76	--	80.03	7.21	--	87.24	66.24

It was observed that ~ 91 % selectivity to amines is obtained at a molar ratio of 1 : 6 at a high conversion of alcohol (~ 76 %) such that ~ 70 % of alcohol is converted to amines. This is attributed to the facilitation of the ammonolysis reaction of alcohol to a high extent such that dehydration activity of alcohol to give 2-butene is suppressed to a large extent (~ 8 % selectivity) and dehydrogenation of alcohol being completely eliminated. It is observed that the ~ 91 % selectivity towards amines comprised largely of sec-butylamine (~ 80 %). Thus the composite catalyst 20%HPWA/HY was found to exhibit a higher catalytic activity than HY zeolite and was also highly selective towards sec-butylamine.

The catalytic activity of different HPWA/HY composite catalyst samples was screened at a temperature of 400 °C, LHSV of 1.00 h^{-1} and a molar ratio of alcohol to ammonia of 1 : 6 as can be seen in Table 4.22.

Table 4.22 Catalytic activity of HPWA/HY catalysts of different compositions for ammonolysis reaction of sec-butyl alcohol

Weight of catalyst = 5 g

Temperature = 400 °C

LHSV = 1.00 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 6

TOS = 1 h

Catalyst	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
10%HPWA/HY	70.18	22.26	1.47	62.54	13.73	--	76.27	53.52
20%HPWA/HY	76.43	8.76	--	80.55	10.69	--	91.24	69.73
30%HPWA/HY	**82.84**	**11.59**	**--**	**60.53**	**18.12**	**9.76**	**88.41**	**73.23**
40%HPWA/HY	83.98	29.58	--	43.17	18.98	8.27	70.42	59.14

The conversion of alcohol increased with increase in HPWA content of composite catalysts. The percentage conversion increased from ~ 70 % to ~ 84 % when HPWA content was increased from 10 % to 40 %. However the catalyst 40%HPWA/HY exhibited a very high dehydration activity (~ 29 %) thereby lowering the conversion of alcohol to amines. The highest conversion of alcohol to amines was obtained over 30%HPWA/HY zeolite where in ~ 73 % conversion of sec-butyl alcohol to amines took place. This high catalytic activity is attributed to a low dehydration activity (~ 11 %), which resulted in a high selectivity towards amines. It was also interesting to note that the composite catalyst 30%HPWA/HY exhibited a significantly high selectivity towards di-sec-butylamine and tri-sec-butylamine even at a very high alcohol to ammonia molar ratio of 1 : 6 where in a high selectivity towards sec-butylamine was expected. Hence the catalytic activity of 30%HPWA/HY catalyst was further investigated for temperature, LHSV and alcohol to ammonia molar ratio variations in order to optimise the conditions to obtain the best yields of amines. The effect of temperature on ammonolysis reaction of sec-butyl alcohol over 30% HPWA/HY composite catalyst is shown in Table 4.23.

Table 4.23 Effect of temperature on ammonolysis reaction of sec-butyl alcohol over 30%HPWA/HY catalyst.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar Ratio (alcohol : NH_3) = 1 : 6

TOS = 1 h

Temp. (°C)	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
300	75.18	11.49	1.94	46.12	25.82	14.63	86.57	65.08
350	**80.59**	**6.75**	**1.17**	**44.77**	**38.73**	**8.58**	**92.08**	**74.20**
400	82.84	11.59	--	60.53	18.12	9.76	88.41	73.23
430	86.12	42.40	--	40.30	10.17	7.13	57.60	49.60

Very high selectivites were observed towards amines except at 430 °C. Also the conversions of alcohol were high. Thus ~ 74 % of sec-butyl alcohol was converted to amines at a temperature of 350 °C. At 430 °C, the conversion of alcohol reached a maximum of ~ 86 % but a high selectivity towards 2-butene (~ 42 %) decreased the overall yields of amines. An interesting result was that the composite catalyst exhibited an improved selectivity towards di-sec-butylamine at relatively lower temperatures. Further investigation of this aspect was carried out by studying the effect of flow rate of the reactants (LHSV variations) at a temperature of 350 °C as shown in Table 4.24.

Table 4.24 Effect of LHSV on ammonolysis reaction of sec-butyl alcohol over 30%HPWA/HY catalyst.

Weight of catalyst = 5 g

Temperature = 350 °C

Molar Ratio (alcohol : NH_3) = 1 : 6

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
0.50	**85.42**	**6.31**	**1.74**	**27.80**	**50.13**	**14.02**	**91.95**	**78.54**
1.00	80.59	6.75	1.17	44.77	38.73	8.58	92.08	74.20
1.50	69.78	21.37	--	42.40	29.08	7.15	78.63	54.86

A maximum of ~ 78 % conversion of sec-butyl alcohol to amines is obtained at a LHSV of 0.50 h^{-1}. It is observed that the selectivity towards di-sec-butylamine and tri-sec-butylamine is enhanced greatly under this condition. At a higher LHSV of 1.50 h^{-1}, the catalyst showed a higher selectivity towards sec-butylamine at the cost of di- and tri- sec-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 [84].

The effect of alcohol to ammonia molar ratio variations on the ammonolysis reaction of sec-butyl alcohol over 30%HPWA/HY catalyst is shown in Table 4.25.

Table 4.25 Effect of molar ratio on ammonolysis reaction of sec-butyl alcohol over 30%HPWA/HY catalyst.

Weight of catalyst = 5 g

Temperature = 350 °C

LHSV = 0.50 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution					% S amines	% C alcohol to amines
		2-Butene	Ethyl methyl ketone	sBA	sDBA	sTBA		
1 : 3	87.13	18.17	--	6.92	49.13	25.58	81.63	71.12
1 : 4	**88.49**	**9.06**	--	**7.57**	**72.83**	**10.14**	**90.44**	**80.03**
1 : 5	84.89	11.41	--	25.98	49.64	12.27	88.59	75.20
1 : 6	85.42	8.05	--	27.80	50.13	14.02	91.95	78.54

Very high conversions of alcohol (> 85 %) are obtained under all conditions and also the selectivities towards amines are also very high. The highest conversion of alcohol to amines is obtained at an alcohol to ammonia molar ratio of 1: 4. ~ 80 % of sec-butyl alcohol gets converted to amines at an alcohol to ammonia molar ratio of

1 : 4 which comprises largely of di-sec-butylamine (~ 72 %). The selectivity to 2-butene is very low (~ 9 %) and formation of ethyl methyl ketone is not observed under this condition. Thus the composite catalyst 30%HPWA/HY was found to be a highly efficient catalyst for the ammonolysis reaction of sec-butyl alcohol having a very high selectivity towards di-sec-butylamine.

The composite catalyst 20%HPWA/HY was found to be highly active catalyst for the synthesis of sec-butylamine by ammonolysis of sec-butyl alcohol. The catalyst showed ~ 70 % conversion of alcohol to amines with a high selectivity towards n-butylamine at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 6.

Thus the composite catalyst 30%HPWA/HY was found to be the most active catalyst for the ammonolysis reaction of sec-butyl alcohol showing ~ 80 % conversion of alcohol to amines with a high selectivity towards di-sec-butylamine at a temperature of 350 °C, LHSV of 0.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4.

Time on stream studies were carried out over these two active catalysts i.e. 20%HPWA/HY and 30%HPWA/HY to study the variations of catalytic activity with time. The time on stream studies over 20%HPWA/HY catalyst at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 6 are shown in Figure 4.5 and the selectivity towards individual amines in a total yield of amines over 20%HPWA/HY catalyst at different TOS is shown in in Figure 4.6.

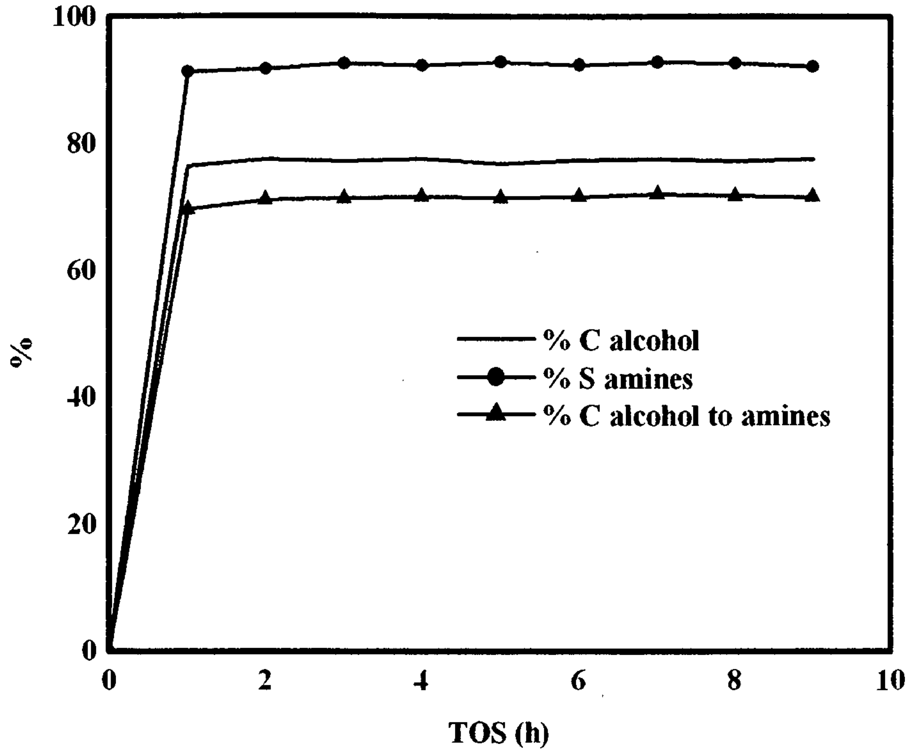

Figure 4.5 Time on stream studies for the ammonolysis reaction of sec-butyl alcohol over 20%HPWA/HY catalyst.

Weight of catalyst = 5 g   Temperature = 350 °C

LHSV = 1.00 h^{-1} Molar Ratio (alcohol : NH_3) = 1 : 6

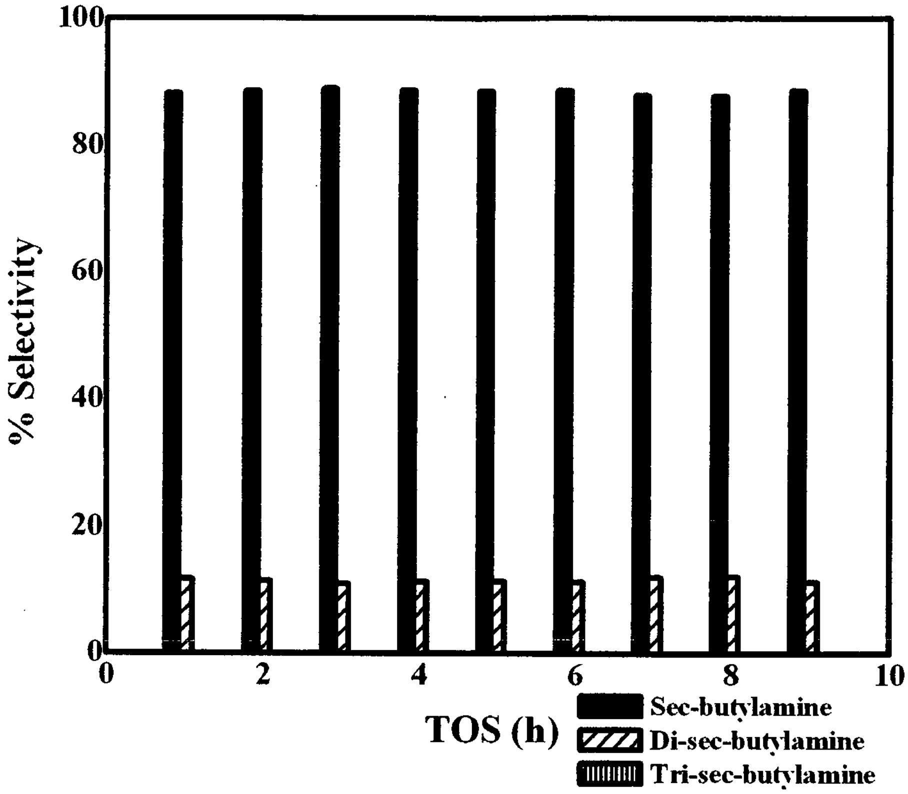

Figure 4.6 Percentage of individual amines in total amount of amines over 20%HPWA/HY catalyst at different TOS.

Weight of catalyst = 5 g	Temperature = 350 °C
LHSV = 1.00 h^{-1}	Molar Ratio (alcohol : NH_3) = 1 : 6

The activity of the catalyst increased by ~ 1 % by the second hour and then remains constant for a period of 9 hours. ~ 71 % of alcohol is converted to amines by the ninth hour. Thus it is observed that the catalytic activity remains constant for about 9 hours. Also from Figure 4.6 it is seen that the selectivities towards sec-butylamine and di-sec-butylamine are almost constant till the ninth hour. Thus the composite catalyst 20%HPWA/HY is found to be highly efficient catalyst for the selective synthesis of sec-butylamine by the ammonolysis reaction of sec-butyl alcohol.

The time on stream studies over 30%HPWA/HY catalyst over a period of 8 hours is shown in Figure 4.7 and the percentage selectivity to individual amines in a total yield of amines at different TOS is shown in Figure 4.8.

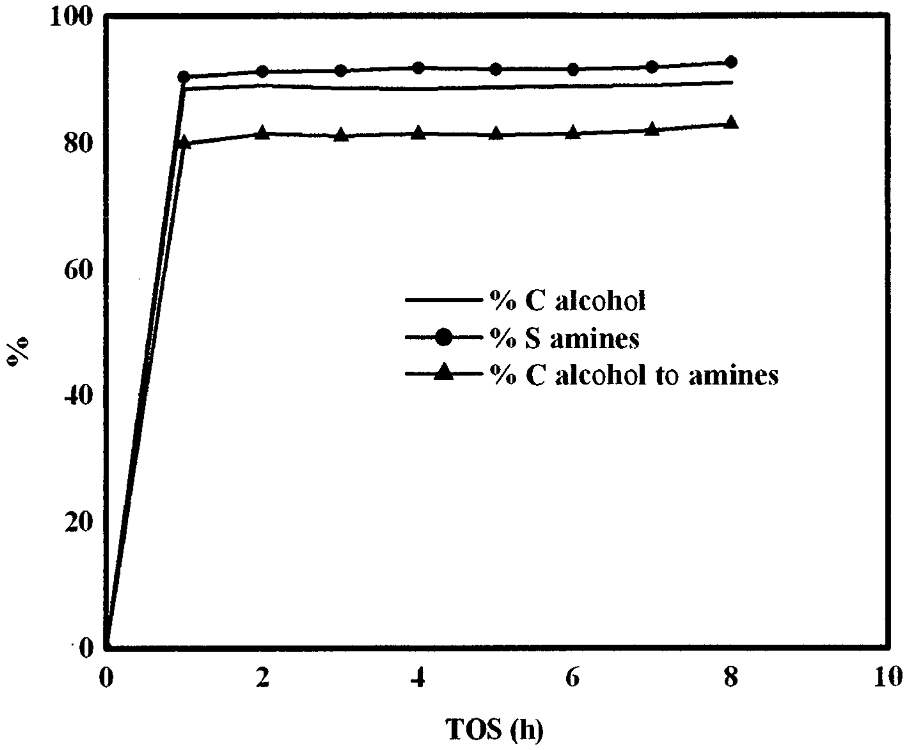

Figure 4.7 Time on stream studies for the ammonolysis reaction of sec-butyl alcohol over 30%HPWA/HY catalyst.

Weight of catalyst = 5 g Temperature = 350 °C

LHSV = 0.50 h^{-1} Molar Ratio (alcohol : NH_3) = 1 : 4

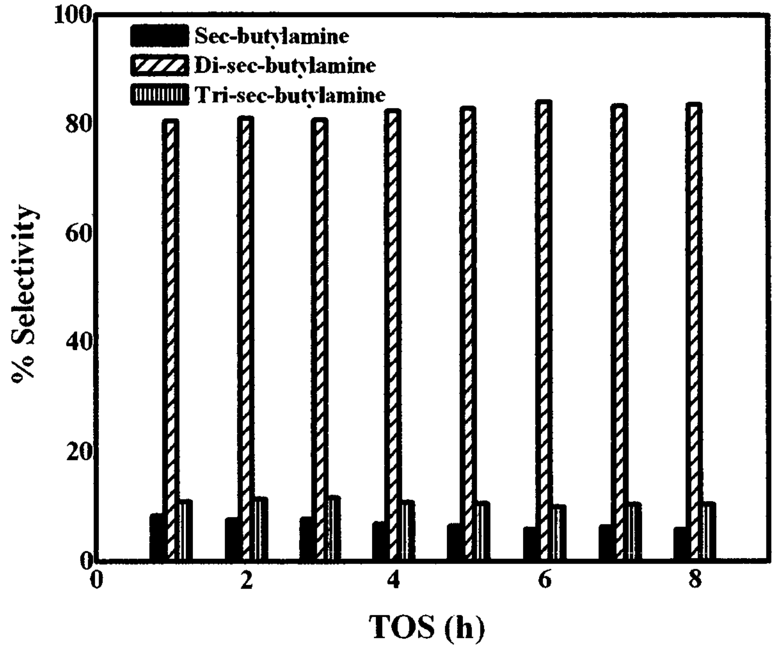

Figure 4.8 Percentage of individual amines in total amount of amines over 30%HPWA/HY catalyst at different TOS.

Weight of catalyst = 5 g	Temperature = 350 °C
LHSV = 0.50 h^{-1}	Molar Ratio (alcohol : NH_3) = 1 : 4

Percentage conversion increased by ~ 1 % over a period of 8 hours. Also the total selectivity towards amines increased by ~ 2 %. Thus ~ 3 % rise in overall yields of amines was obtained by the eighth hour. Also from Figure 4.8 it can be seen that the selectivity towards di-sec-butylamine increases by ~ 3 % by the eighth hour. Thus the catalyst showed an improved performance with time. Thus the composite catalyst 30%HPWA/HY is found to be highly efficient catalyst for the selective synthesis of di-sec-butylamine by the ammonolysis reaction of sec-butyl alcohol.

4.7 Correlation of catalytic activity with acidity of catalysts

A comparison of the data obtained over HY, HPWA and 20%HPWA/HY showed that the composite catalyst 20%HPWA/HY exhibited a much higher catalytic activity for the ammonolysis reaction in comparison to the individual catalysts. The total acidity of the mixed catalyst is lower compared to both the individual catalysts. This indicates that all the acid sites are not active for the ammonolysis reaction. The fact that HY zeolite with a comparatively lower total acidity showed a superior activity compared to that of more acidic Hβ and HZSM-5(40) zeolites supports our view. To get an insight into the active sites, which lead to a higher catalytic activity of the composite catalyst 20%HPWA/HY over HPWA and HY zeolite, the acidity profiles of the three catalysts were closely studied. The acidity profiles showed that composite catalysts. 20%HPWA/HY had a significantly higher relative concentration of acid sites beyond 320 °C compared to individual catalysts. Thus it was evident that a higher proportion of strong acid sites in the composite catalyst led to an improvement of catalytic activity over the individual catalysts.

A comparison of the active catalysts 4 with respect to catalytic activity and selectivity under their highest yield conditions is shown in Table 4.26 in relation with ther acidity data.

Table 4.26 Comparison of catalytic activity, selectivity and acidity of the various catalysts

Catalyst	% C alcohol	% S 2-butene	% S amines	% C alcohol to amines	Total acidity (mmol / g)	% Acidity beyond 320 °C
HZSM-5(40)	48.90	33.06	64.62	31.60	0.47371	10.66
HY	68.81	14.33	85.67	58.95	0.38525	33.35
Hβ	62.13	20.87	79.13	49.16	0.48694	23.68
HPWA	65.07	51.12	48.88	31.80	0.50115	21.20
20%HPWA/HY	76.43	8.76	91.24	69.73	0.35528	36.08
30%HPWA/HY	88.49	9.06	90.44	80.03	0.39413	43.06

Figure 4.9 shows a correlation between percentage conversion of alcohol to amines and relative concentration of strong acid sites.

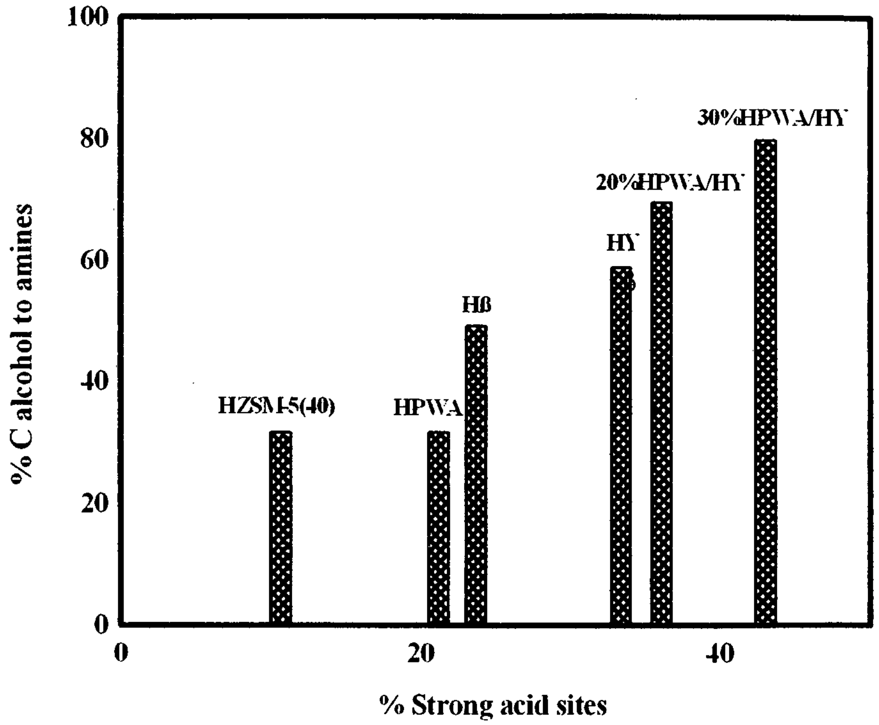

Figure 4.9 Correlation between percentage conversion of alcohol to amines and relative concentration of strong acid sites.

It is seen that the percentage conversion of alcohol to amines increases with a corresponding increase in relative concentration of strong acid sites for the various active catalysts. A higher relative proportion of strong acid sites favours a high conversion of alcohol to amines leading to a higher catalytic activity.

3.8 Conclusions

1. ZSM-5, Y, β zeolites and phosphotungstic acid are investigated as catalysts for the ammonolysis of sec-butyl alcohol. The products were sec-butylamine, di-sec-butylamine and tri-sec-butylamine.
2. It is observed that the variation of Si/Al ratio of HZSM-5 zeolite has a pronounced effect on the catalytic activity. For the three different HZSM-5 zeolite viz. HZSM-5(40), HZSM-5(80) and HZSM-5(225), it is observed that percentage selectivity to amines and percentage conversion of alcohol to amines decreased as Si/Al ratio increased.
3. The catalytic activity for Y zeolites followed the order NaY < ZnY < NiY < CuY < HY.
4. The catalytic activity for β zeolites followed the order Naβ < Niβ < Cuβ < Znβ < Hβ. The best yields over Hβ zeolite are obtained at a temperature of 400 °C, LHSV of 2.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 5 wherein ~ 62 % overall conversion of the alcohol occurs at ~ 80 % selectivity towards amines out of which ~ 65 % is sec-butylamine.
5. HPWA exhibited a poor activity for the formation of amines. It behaved more as a catalyst for dehydration of alcohol.
6. The composite catalyst 20%HPWA/HY was found to be highly active catalyst for the synthesis of sec-butylamine. The catalyst showed ~ 70 % conversion of alcohol to amines with a high selectivity towards sec-butylamine at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 6.

7. The composite catalyst 30%HPWA/HY was found to be the most active catalyst and showed a high selectivity towards di-sec-butylamine. Highest conversion of alcohol to amines (~ 80 %) was observed at a temperature of 350 ^{o}C, LHSV of 0.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4.

8. A higher relative proportion of strong acid sites favoured a high conversion of alcohol to amines.

Chapter 5

Ammonolysis of t-butyl alcohol

Ammonolysis of t-butyl alcohol

This Chapter describes the catalytic activity of various catalysts for the synthesis of t-butylamine by ammonolysis reaction of t-butyl alcohol both with anhydrous as well as aqueous ammonia. The reactor set up for the ammonolysis reaction of t-butyl alcohol using anhydrous ammonia gas is similar to that used for the ammonolysis reaction of n-butyl alcohol. The ammonolysis reaction of t-butyl alcohol is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia over ZSM-5, Y and β zeolites and phosphotungstic acid. The products were analysed by gas chromatography with a Chemito 8610 HT gas chromatograph using a carbowax 20 M KOH treated column.

The reaction is investigated to find a catalyst that would give selective production of t-butylamine in high yields and at the same time suppress the formation of isobutene. The catalytic activity is correlated to the catalyst characteristics.

5.1 Ammonolysis with anhydrous ammonia over zeolite catalysts

HZSM-5(40) was taken as a model catalyst to optimise the conditions for the comparison of catalytic activity of various zeolite catalysts.

The effect of temperature on ammonolysis reaction of t-butyl alcohol over HZSM-5(40) zeolite at a LHSV of 2.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4 is shown in Table 5.1.

Table 5.1 Effect of temperature on ammonolysis reaction of t-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

LHSV = 2.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temperature (°C)	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
200	26.45	89.93	10.07	2.66
250	39.78	85.12	14.88	5.92
280	**48.84**	**76.19**	**23.81**	**11.63**
300	54.08	87.43	12.57	6.80
350	65.95	90.08	9.92	6.54

As the temperature increases the conversion of alcohol increases. However, the highest conversion of t-butyl alcohol to t-butyl amine is obtained at a temperature of 280 °C (~ 12 %). At higher temperatures dehydration of alcohol becomes prominent. When this data was compared with the data of n-butyl alcohol and sec-butyl alcohol it was observed that a high conversion of t-butyl alcohol takes place as compared to the other two alcohols at comparatively lower temperatures, which could be related to the reactivity of the three isomeric butyl alcohols (tertiary alcohols are more reactive than corresponding primary and secondary alcohols) towards dehydration process.

The effect of LHSV on the ammonolysis reaction at 280 °C is shown in Table 5.2.

Table 5.2 Effect of LHSV on ammonolysis reaction of t-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

Temperature = 280 °C

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
0.50	58.85	79.88	20.12	11.84
1.00	**55.46**	**63.87**	**36.13**	**20.04**
1.50	51.42	71.91	28.09	14.44
2.00	48.84	76.19	23.81	11.63
2.50	42.56	77.92	22.08	9.40
3.00	38.17	81.43	18.57	7.09

The highest conversion of alcohol to t-butylamine (~ 20 %) is obtained at a LHSV of 1.00 h^{-1}.

Table 5.3 shows the effect of alcohol to ammonia molar ratio variations over HZSM-5(40) zeolite catalyst.

Table 5.3 Effect of molar ratio on ammonolysis reaction of t-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

Temperature = 280 °C

LHSV = 1.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
1 : 3	52.08	65.21	34.79	18.12
1 : 4	55.46	63.17	36.13	20.04
1 : 5	43.95	59.98	40.02	17.59
1 : 6	40.08	66.12	33.88	13.58

The highest conversion of alcohol to ammonia was obtained at an alcohol to ammonia molar ratio of 1 : 4 wherein ~ 20 % yield of t-butylamine was obtained.

Thus the best yield over HZSM-5(40) was obtained at a temperature of 280 °C, LHSV of 1.00 h^{-1} and molar ratio of alcohol to ammonia of 1 : 4. The catalytic activity of various ZSM-5 zeolite catalysts was evaluated under these conditions. The data is shown in Table 5.4.

Table 5.4 Catalytic activity of various catalysts for ammonolysis reaction of t-butyl alcohol.

Weight of catalyst = 5 g

Temperature = 280 °C LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Catalyst	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
HZSM-5(40)	**55.46**	**63.87**	**36.13**	**20.04**
HZSM-5(80)	48.17	68.13	31.87	15.35
HZSM-5(225)	30.95	72.07	27.93	8.64
NaZSM-5	12.95	66.91	33.09	4.29
CuZSM-5	29.05	59.13	40.87	11.87
NiZSM-5	**43.08**	**54.18**	**45.82**	**19.74**
ZnZSM-5	23.18	72.85	27.15	6.29
NaY	12.09	100	--	--
HY	**46.12**	**78.17**	**21.83**	**10.07**
CuY	12.58	100	--	--
NiY	**24.02**	**62.36**	**37.64**	**9.04**
ZnY	21.14	79.82	20.18	4.27
Naβ	12.74	100	--	--
Hβ	**43.85**	**76.38**	**23.62**	**10.36**
Cuβ	34.69	95.16	4.84	1.68
Niβ	**49.77**	**80.21**	**19.79**	**9.85**
Znβ	22.19	67.82	32.18	7.14

It is seen from Table 5.4 that from among the severl catalysts investigated only the ZSM-5 zeolites showed significantly higher catalytic activities. It is observed that among the three HZSM-5 zeolites of different Si/Al ratios HZSM-5(40) zeolite having highest total acidity showed the highest catalytic activity. This shows that the catalytic activity is influenced by the acidity of the catalyst. The maximum activity among all the catalyst screened under these conditions was shown by HZSM-5(40) of ~ 20 %. Among the Y and β zeolites the protonic forms of zeolite i.e. HY and Hβ showed the highest catalytic activity. Nickel ion exchanged zeolites, i.e. NiZSM-5, NiY and Niβ showed activities comparable to that of protonic zeolites. Among the three HZSM-5 zeolites of different Si/Al ratios it can be seen that the conversion of alcohol decreases considerably with increase in Si/Al ratios where as the selectivity to t-butylamine is almost similar. Thus we can conclude that the decrease in number of H^+ ions is playing a significant role here. For all the catalysts, the conversion of alcohol could be related to total acidity. Catalysts with a higher total acidity showed higher conversions of t-butyl alcohol.

NiZSM-5 (SiAl = 40) showed a catalytic activity comparable to that of HZSM-5(40) zeolite and also a better selectivity towards t-butylamine. Therefore the ammonolysis reaction of t-butyl alcohol was further investigated over NiZSM-5 zeolite to optimize the conditions to obtain the best yields of t-butylamine.

The effect of temperature on the ammonolysis reaction was investigated at a LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4 is shown in Table 5.5.

Table 5.5 Effect of temperature on ammonolysis reaction of t-butyl alcohol over NiZSM-5 zeolite.

Weight of catalyst = 5 g

LHSV = 1.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

Temperature (^{0}C)	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
250	40.01	57.97	42.03	16.82
280	43.08	54.18	45.82	19.74
300	49.94	52.25	47.25	23.60
320	**51.75**	**50.83**	**49.17**	**25.45**
350	52.17	61.88	38.12	19.89
400	55.38	73.51	26.49	14.67

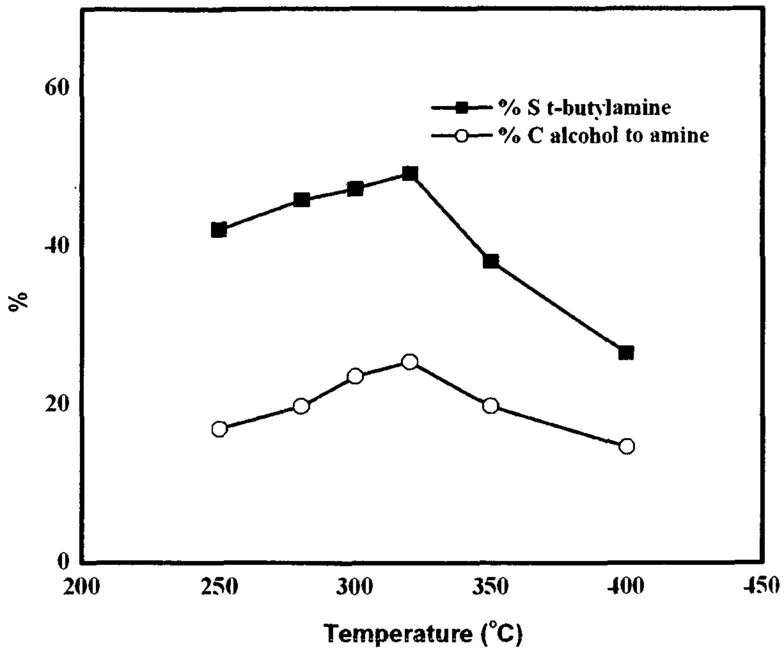

Figure 5.1 Effect of temperature on ammonolysis reaction of t-butyl alcohol over NiZSM-5 zeolite.

Weight of catalyst = 5 g	LHSV = 1.00 h^{-1}
Molar ratio (alcohol : NH_3) = 1 : 4	TOS = 1 h

The percentage conversion increased with increase in temperature however a maximum conversion of t-butyl alcohol to t-butylamine was obtained at a temperature of 320 °C where in ~ 25 % conversion of t-butyl alcohol to t-butylamine was observed. Above this temperature a high dehydration activity led to lowered selectivity towards t–butylamine.

The reaction at relatively lower temperatures could be due to Langmuir – Hinshelwood mechanism between the co-adsorbed alcohol and ammonia. Beyond 320 °C as $NH_{3(g)}$ is desorbed, Langmuir – Hinshelwood mechanism is not operative and gas phase NH_3 is probably les effective for any intermolecular dehydration to occur. Hence above 320 °C, the selectivity towards t–butylamine is lowered.

The effect of LHSV on the ammonolysis reaction of t-butyl alcohol over NiZSM-5 zeolite is shown in Table 5.6.

Table 5.6 Effect of LHSV on ammonolysis reaction of t-butyl alcohol over NiZSM-5 zeolite.

Weight of catalyst = 5 g

Temperature = 320 °C

Molar ratio (alcohol : NH_3) = 1 : 4

TOS = 1 h

LHSV	% C	% Product distribution		% C
(h^{-1})	alcohol	isobutene	t-butylamine	alcohol to amine
0.50	54.73	58.02	41.98	22.98
1.00	51.75	50.83	49.17	25.45
1.25	50.42	47.54	52.46	26.45
1.50	**49.68**	**43.08**	**56.92**	**28.28**
1.75	44.35	45.78	54.22	24.05
2.00	42.27	48.65	51.35	21.71
2.50	38.59	57.34	42.66	16.46

It is seen that with increase in LHSV from 0.50 h^{-1} to 2.50 h^{-1} the percentage conversion decreases from ~ 55 % to ~ 39 %. However differential selectivities towards t-butylamine are obtained at different LHSVs, which suggest that the overall yields of the ammonolysis reaction depends on the contact time of the reactants over the catalyst. Thus it can be seen that at a LHSV of 2.00 h^{-1} and 2.50 h^{-1} wherein although the percentage selectivity to t-butylamine is almost the same as that at 1.50 h^{-1}, the conversion of t-butyl alcohol to t-butylamine is reduced due to low overall conversion of t-butyl alcohol. The differential conversions and selectivities obtained at different LHSVs suggest that dehydrative mechanism is operative here i. e. intermolecular dehydration of t-butyl alcohol and ammonia leads to formation of t-butylamine. If t-butylamine was formed by the subsequent addition of ammonia to isobutene, one would expect increasing yields of t-butylamine as LHSV is lowered i. e. at longer contact times of reactants over the catalyst, wherein there would be a higher probability of addition of ammonia to isobutene as the initially formed alkene would spend longer times on the catalyst to further react with ammonia. However we observe at LHSVs lower than 1.50 h^{-1}, the yields of t-butylamine are lowered. Thus ammonolysis reaction is likely to occur through an intermolecular dehydration of t-butyl alcohol and ammonia leading to formation of t-butylamine.

The effect of alcohol to ammonia molar ratio on the ammonolysis reaction of t-butyl alcohol over NiZSM-5 zeolite is shown in Table 5.7.

Table 5.7 Effect of molar ratio on ammonolysis reaction of t-butyl alcohol over NiZSM-5 zeolite.

Weight of catalyst = 5 g

Temperature = 320 °C

LHSV = 1.50 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution isobutene	 t-butylamine	% C alcohol to amine
1 : 2	55.02	50.91	49.09	27.01
1 : 3	**53.67**	**43.88**	**56.12**	**30.12**
1 : 4	49.68	43.08	56.92	28.28
1 : 5	46.13	46.20	53.80	24.82
1 : 6	42.12	50.22	49.78	20.97

The highest conversion of t-butyl alcohol to t-butylamine is obtained at an alcohol to ammonia ratio of 1 : 3 where in ~ 30 % conversion of t-butyl alcohol to t-butylamine is obtained. Thus the NiZSM-5 zeolite showed a higher activity for the synthesis of t-butylamine as compared to HZSM-5(40) zeolite.

5.2 Ammonolysis with anhydrous ammonia over phosphotungstic acid (HPWA)

The catalytic activity of HPWA catalyst was tested for the ammonolysis reaction of t-butyl alcohol. The effect of temperature on the ammonolysis reaction of t-butyl alcohol over HPWA catalyst is shown in Table 5.8.

Table 5.8 Effect of temperature on ammonolysis reaction of t-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

LHSV = 2.00 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 3

TOS = 1 h

Temperature (°C)	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
250	64.03	96.86	3.14	2.01
280	**68.17**	**92.70**	**7.30**	**4.98**
300	74.14	100	--	--
350	80.47	100	--	--

Very low yields of t-butylamine were obtained at 280 °C. At temperatures of 300 °C and above, 100 % selectivity towards the dehydration of t-butyl alcohol to isobutene was observed.

The effect of LHSV on the ammonolysis reaction of t-butyl alcohol over HPWA catalyst is shown in Table 5.9.

Table 5.9 Effect of LHSV on ammonolysis reaction of t-butyl alcohol over HPWA catalyst.

Weight of catalyst = 5 g

Temperature = 280 °C

Molar ratio (alcohol : NH_3) = 1 : 3

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
1.50	74.08	93.03	6.97	5.17
2.00	68.17	92.70	7.30	4.98
2.50	**65.92**	**88.41**	**11.59**	**7.64**
3.00	60.13	96.48	3.52	2.12

Very low yields were obtained owing to a very high dehydration activity to give isobutene. A maximum of ~ 8 % of the alcohol was converted to t-butylamine.

5.3 Ammonolysis with anhydrous ammonia over 20%HPWA/NiZSM-5 composite catalyst

A composite catalyst 20%HPWA/NiZSM-5 was prepared as shown in Section 2.1.2 and the catalytic activity of the catalyst was evaluated for the ammonolysis reaction.

The effect of temperature on the ammonolysis reaction of t-butyl alcohol over 20%HPWA/NiZSM-5 catalyst is shown in Table 5.10.

Table 5.10 Effect of temperature on ammonolysis reaction of t-butyl alcohol over HPWA/NiZSM-5 catalyst.

Weight of catalyst = 5 g

LHSV = 1.50 h^{-1}

Molar ratio (alcohol : NH_3) = 1 : 3

TOS = 1 hr

Temperature (°C)	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
280	61.71	76.04	23.96	14.79
300	**66.28**	**72.82**	**27.18**	**18.02**
320	69.13	78.81	21.19	14.65
340	73.58	87.60	12.40	9.13

A ~ 18 % conversion of t-butyl alcohol to t-butylamine was obtained at a temperature of 300 °C. The low yields of t-butylamine were largely due to high selectivity towards the dehydration product i.e. isobutene, although higher conversions were obtained as compared to pure NiZSM-5 zeolite.

The effect of LHSV on the ammonolysis reaction of t-butyl alcohol over 20%HPWA/NiZSM-5 catalyst is shown in Table 5.11.

Table 5.11 Effect of LHSV on ammonolysis reaction of t-butyl alcohol over HPWA/NiZSM-5 catalyst.

Weight of catalyst = 5 g

Temperature = 300 °C

Molar ratio (alcohol : NH_3) = 1 : 3

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
1.00	74.32	80.94	19.06	14.17
1.50	**66.28**	**72.82**	**27.18**	**18.02**
2.00	62.98	68.60	31.40	19.78
2.50	59.37	82.25	17.75	10.54

The LHSV variations could not improve the yields of t-butylamine by a large extent. A maximum of 19.78 % conversion of t-butyl alcohol to t-butylamine was achieved at a LHSV of 2.00 h^{-1}.

The effect of alcohol to ammonia molar ratio variation on the ammonolysis reaction of t-butyl alcohol over 20%HPWA/NiZSM-5 catalyst is shown in Table 5.12.

Table 5.12 Effect of molar ratio on ammonolysis reaction of t-butyl alcohol over HPWA/NiZSM-5 catalyst.

Weight of catalyst = 5 g

Temperature = 300 °C

LHSV = 2.00 h^{-1}

TOS = 1 h

Molar ratio Alcohol : NH_3	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
1 : 1	69.17	74.92	25.08	17.34
1 : 2	**67.24**	**67.60**	**32.40**	**21.79**
1 : 3	62.98	68.60	31.40	19.78
1 : 4	63.47	73.98	26.02	16.52
1 : 5	60.51	82.52	17.48	10.58

The lowering of molar ratio from 1 : 3 to 1 : 2 improved the yields of t-butylamine up to about 22 %. However the yields were lower compared to pure NiZSM-5 zeolite. Thus it is seen that HPWA modification does not help to improve the yields of t-butylamine.

5.4 Mechanistic studies

5.4.1 Effect of nickel concentration on catalytic activity

To study the effect of amount of Ni^{+2} ions in NiZSM-5 zeolite on the ammonolysis reaction, NiZSM-5(225) was prepared by ion exchange of HZSM-5(225) with nickel nitrate. The catalyst NiZSM-5(225) contained a lower concentration of Ni^{+2} ions [%Ni^{+2} = 0.62 %] compared to NiZSM-5(40) [%Ni^{+2} = 1.37 %] as can be seen from Table 2.3. The catalytic activity of the catalyst was tested for the ammnolysis reaction of t-butyl alcohol. Figure 5.2 shows the comparative catalytic activities of NiZSM-5(40) and NiZSM-5(225) zeolite catalysts.

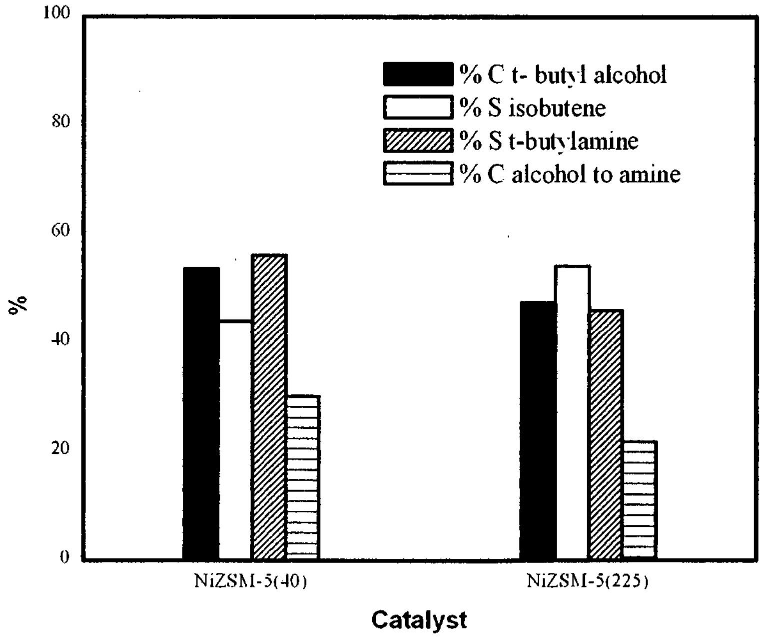

Figure 5.2 Catalytic activity of NiZSM-5(40) and NiZSM-5(225) for the ammonolysis reaction of t-butyl alcohol.

Weight of catalyst = 5 g	Temperature = 320 °C
LHSV = 1.50 h^{-1}	Molar ratio (alcohol : NH_3) = 1 : 3

The catalyst NiZSM-5 (Si/Al = 225) showed a lower catalytic activity as compared to NiZSM-5 zeolite (Si/Al =40). This indicates that the Ni^{+2} ions in NiZSM-5 zeolite could be an active vehicle for the ammonolysis reaction of t-butyl alcohol along with the acidity of the catalyst. Also the high activities shown by NiY and Niβ (comparable to protonic form of the corresponding zeolite) suggest that Ni ions may play an important role in catalytic activity.

5.4.2 Effect of presence of water in reaction feed on catalytic activity

To study the effect of presence of water in the feed, a series of experiments were performed with varying moles of water in the feed at a constant alcohol to ammonia ratios over NiZSM-5 zeolite at the optimum yield conditions. Figure 5.3 shows the catalytic activity of NiZSM-5 zeolite at varying amounts of water in the feed. (The data for absence of water in the feed (0 moles of water) is taken from Table 5.7).

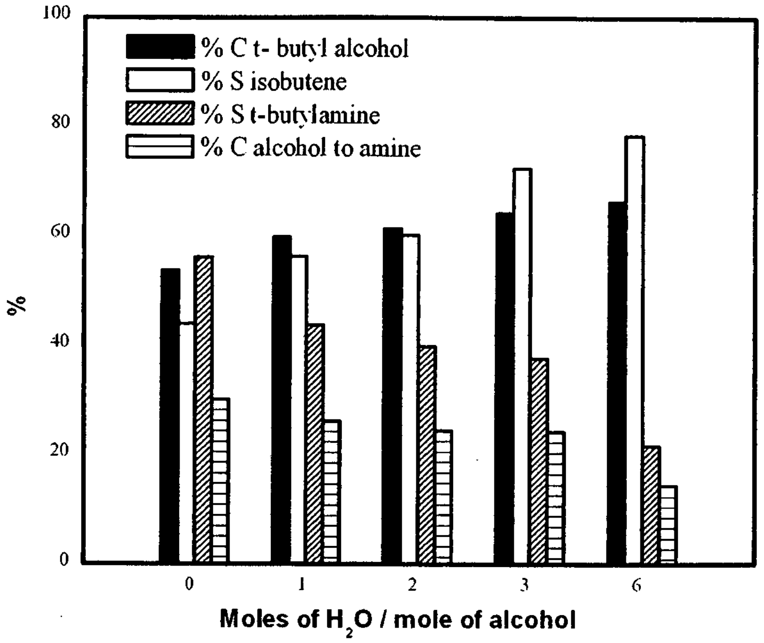

Figure 5.3 Catalytic activity of NiZSM-5 zeolite in the presence and absence of water in the feed.

Weight of catalyst = 5 g	Temperature = 320 °C
LHSV = 1.50 h^{-1}	Molar ratio (alcohol : NH_3) = 1 : 3
TOS = 1 h	

It was observed that the conversions of t-butyl alcohol increased with an increase in amount of water in the feed. However the selectivity towards t-butylamine decreased with increase in water content with a corresponding increase in selectivity towards isobutene. The presence of water in the feed, which is equivalent to steam treatment of catalysts, which is known to lead to the formation of mobile Bronsted acid sites [294, 295], or formation of some super acidic Bronsted active sites, [296] resulted in lowering the selectivity towards t-butylamine. Thus it seems that the generation of these additional Bronsted sites resulted in lowering the yield of t-butylamine. Figure 5.3 suggests that the conversion of the alcohol over NiZSM-5 zeolite increased in the presence of water in reaction feed under similar reaction conditions in the absence of water in the feed. However the increased conversion resulted in a high dehydration activity resulting in loss of selectivity towards t-butylamine. Thus it looks evident that the Bronsted acid sites are responsible for the dehydration of the alcohol to give isobutene. Further a comparison of the acid profiles of the two active catalysts i. e. HZSM-5(40) and NiZSM-5 as seen from Figure 2.14 and Figure 2.16 showed that HZSM-5 has a higher Bronsted acidity (strong acid sites) compared to NiZSM-5 zeolite. Also a comparison of catalytic activity and acidity profiles of NiZSM-5 and 20%HPWA/NiZSM-5 showed that the composite catalyst had a high amount of Bronsted acidity, which resulted in a lower activity of the composite catalyst due to high dehydration activity. Thus it is clear that the Bronsted acid sites are responsible for the dehydration of the alcohol and the weak acid sites may be the active sites for the ammonolysis reaction. The high conversions of alcohol obtained at lower temperatures as compared to n-butyl alcohol and sec-butyl alcohol, a high dehydrating activity observed at higher temperatures and a higher reactivity of t-butyl alcohol supports the above view that strong acidity may result in loss of catalytic activity for the ammonolysis reaction due to a high dehydrating activity. Our results are similar to that obtained by Bassilli and Baiker [137] for the amination of 1-methoxy-2-propanol over silica supported nickel catalyst. They have concluded that the presence of water helps in increasing the conversion of alcohol but results in lowering of selectivity.

The formation of t-butylamine is also likely to occur through intermolecular dehydration between t-butyl alcohol and ammonia. It is unlikely that a subsequent addition of ammonia to isobutene takes place in this case, as the addition of ammonia to alkenes to give amines is reported to take place usually at higher pressures [20, 21]. Mizuno et. al. [19] have reported the formation of t-butylamine via the reaction of isobutene and ammonia at atmospheric pressure over zeolite catalysts. However they have reported longer equilibrium times (~ 2 hours) for the formation of products. We have been able to detect the formation of t-butylamine within a short time from the start of the reaction, which suggests that the formation of t-butylamine occurs through the intermolecular dehydration between t-butyl alcohol and ammonia Also Bronsted acid sites are reported to be the active sites for the ammonolysis reaction in the above report i. e. the addition of ammonia to alkene. If that was the case we would have obtained a higher yield of t-butylamine upon presence of water in the feed as it is bound to increase the Bronsted acidity, leading to formation of amines by two pathways. Instead we observe a decrease in catalytic activity, which suggests that the formation of t-butylamine by subsequent addition of ammonia to isobutene is unlikely. However the formation of t-butylamine at much lower temperatures in significant yields suggests that the intermolecular dehydration reaction between the two reactants occurs via Langmuir – Hinshelwood mechanism i .e between co-adsorbed alcohol and ammonia as well as through Eley - Rideal mechanism wherein the ammonia from gas phase could collide with the adsorbed t-butyl alcohol to yield the t-butylamine. The very low yields of t-butylamine observed at higher temperatures (> 320 °C) wherein no substantial ammonia should be present on the catalysts in the adsorbed state indicates that the gas phase ammonia is probably less effective for intermolecular dehydration to occur. Hence the contribution from the latter pathway should be very low in the overall yields of t-butylamine.

5.5 Time on stream studies over NiZSM-5 zeolite

NiZSM-5 was found to be the most active catalyst for the ammonolysis reaction of t-butyl alcohol with anhydrous ammonia. Time on stream studies were carried out over NiZSM-5 zeolite at a temperature of 320 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 3. The data is presented in Figure 5.4.

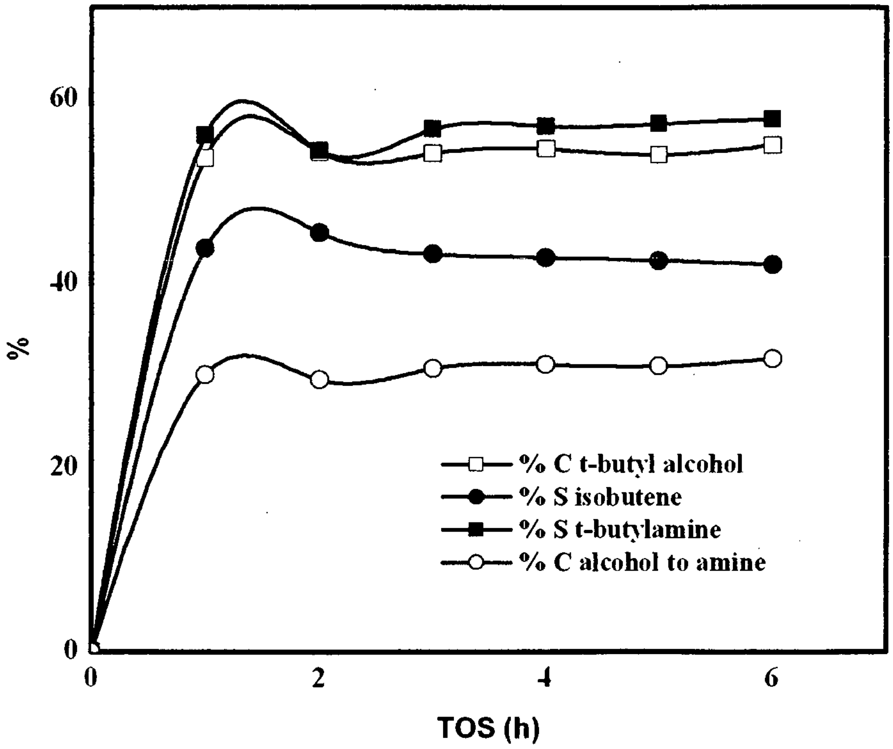

Figure 5.4 Time on stream studies over NiZSM-5 zeolite catalyst.

Weight of catalyst = 5 g	Temperature = 320 °C
LHSV = 1.50 h^{-1}	Molar ratio (alcohol : NH_3) = 1 : 3

The activity increased by about 2 % over a period of 6 hours. The high yields of isobutene did not seem to affect the conversion of t-butyl alcohol or the selectivity towards t-butylamine. This may be attributed to the non-coking properties of ZSM-5 zeolite [73].

5.6 Ammonolysis with aqueous ammonia over zeolite catalysts

HZSM-5(40) was taken as a model catalyst to optimise the conditions for the comparison of catalytic activity of various zeolite catalysts.

The effect of temperature on ammonolysis reaction of t-butyl alcohol with aqueous ammonia over HZSM-5(40) zeolite at a LHSV of 2.00 h^{-1} is shown in Table 5.13. A 1 :2 alcohol to ammonia ratio by volume was used as reaction feed.

Table 5.13 Effect of temperature on ammonolysis reaction of t-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

LHSV = 2.00 h^{-1}

TOS = 1 h

Temperature (°C)	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
200	26.82	57.54	42.46	11.38
250	30.54	58.06	41.94	12.80
280	33.97	63.09	36.91	12.53
300	38.05	63.92	36.08	13.72
320	**42.58**	**65.57**	**34.43**	**14.66**
350	46.75	86.02	13.98	6.53

The percentage conversion increased with increase in temperature. A maximum of ~ 15 % conversion of t-butyl alcohol to t-butylamine is obtained at a temperature of 320 °C. The very high dehydration activity (~ 86 %) observed at 350 °C suggests that acid sites at this temperature i. e. strong acid sites bring about dehydration of t-butyl alcohol as observed in the case of ammonolysis of t-butyl alcohol with anhydrous ammonia.

The effect of LHSV on the ammonolysis reaction of t-butyl alcohol over HZSM-5(40) zeolite is shown in Table 5.14.

Table 5.14 Effect of LHSV on ammonolysis reaction of t-butyl alcohol over HZSM-5(40) zeolite.

Weight of catalyst = 5 g

Temperature = 320 °C

TOS = 1 h

LHSV (h^{-1})	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
0.50	55.07	72.13	27.87	15.35
1.00	51.58	69.75	30.25	15.60
1.50	45.74	67.38	32.62	14.92
2.00	42.58	65.57	34.43	14.66
2.50	**39.09**	**46.95**	**53.05**	**20.74**
3.00	33.05	54.07	45.93	15.18
3.50	31.95	60.83	39.17	12.51

The percentage conversion of alcohol decreased with increasing LHSV. However the selectivity to t-butylamine is highest (53.05 %) at a LHSV of 2.50 h^{-1}. ~ 20 % conversion of t-butyl alcohol to t-butylamine takes place under this condition. The differential conversions and selectivities obtained at different LHSVs suggest that dehydrative mechanism is operative here too. Thus if addition of ammonia to alkene was the likely pathway then one would have expected higher yields of t-butylamine at lower LHSVs (longer contact times of reactants over the catalyst) wherein there would be a higher probability of addition of ammonia to isobutene as the initially formed alkene would spend longer times on the catalyst to further react with ammonia. Thus ammonolysis reaction is likely to occur through an intermolecular dehydration of t-butyl alcohol and ammonia leading to formation of t-butylamine.

The catalytic activity of different catalysts was evaluated at a temperature of 320 °C and a WHSV of 2.50 h^{-1}. The data is presented in Table 5.15.

Table 5.15 Catalytic activity of various catalysts for ammonolysis reaction of t-butyl alcohol

Weight of catalyst = 5 g

Temperature = 320 °C

LHSV = 2.50 h^{-1}

TOS = 1 h

Catalyst	% C alcohol	% Product distribution		% C alcohol to amine
		isobutene	t-butylamine	
HZSM-5(40)	**39.09**	**46.95**	**53.05**	**20.74**
HZSM-5(80)	32.71	53.94	46.06	15.07
HZSM-5(225)	26.48	63.06	36.94	9.78
NaZSM-5	14.08	77.19	22.81	3.21
CuZSM-5	10.07	72.58	27.42	2.76
NiZSM-5	16.12	85.17	14.83	2.39
ZnZSM-5	9.78	78.13	21.87	2.14
NaY	6.54	73.27	26.73	1.75
HY	33.19	91.19	8.81	2.92
CuY	10.58	100	--	--
NiY	15.08	87.37	12.63	1.90
ZnY	12.56	84.07	15.93	2.00
Naβ	9.82	100	--	--
Hβ	37.63	83.92	16.08	6.05
Cuβ	27.58	84.88	15.12	--
Niβ	36.49	81.06	18.94	6.91
Znβ	14.59	79.38	20.62	3.01

It is found that HZSM-5(40) zeolite is the most active catalyst. The yields of t-butylamine obtained are very low in most of the cases (as compared in the case of gas phase NH_3).

Time on stream studies were carried out HZSM-5(40) zeolite catalyst to check the variation of catalytic activity with time. The data is presented in Figure 5.5.

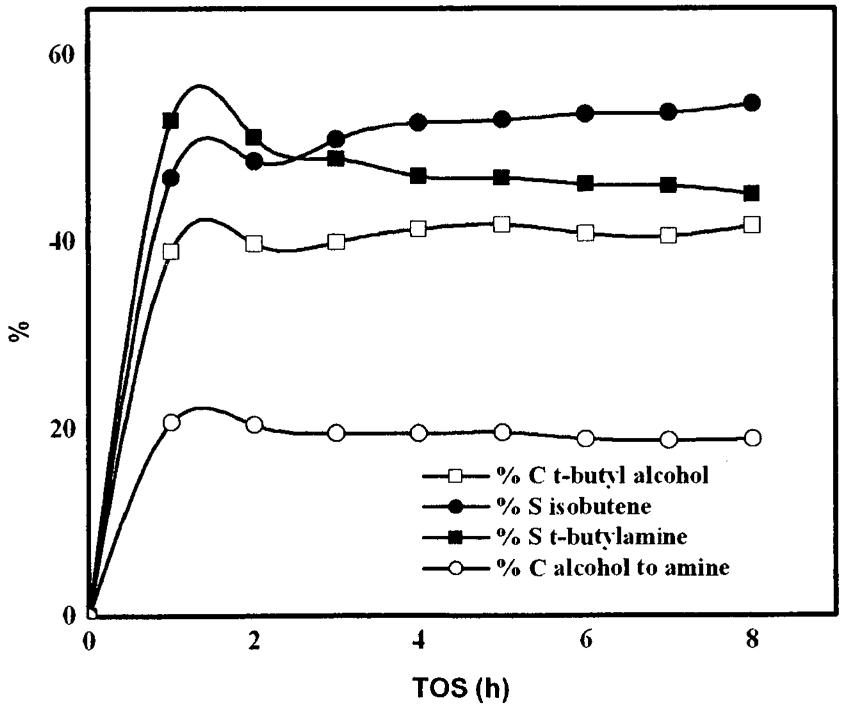

Figure 5.5 Time on stream studies on HZSM-5(40) zeolite catalyst.

Weight of catalyst = 5 g Temperature = 320 °C

LHSV = 2.50 h^{-1}

It is observed from Figure 5.5 that the conversion of alcohol increased over a period of 8 hours however the yields of t-butylamine decreased due to decrease in selectivity towards t-butylamine. One would expect the catalyst to maintain the activity due to its non-coking properties. However it is likely that the generation of additional Bronsted sites due to presence of water as reactant increases the dehydration activity of the catalyst resulting in lowering the yields of t-butylamine. Thus it supports our mechanistic view that Bronsted acid sites catalyse the dehydration of t-butyl alcohol whereas the weak acid sites assist the ammonolysis reaction. Thus it is concluded that the presence of water in the feed increases the conversion of alcohol but decreases the selectivity towards t-butylamine.

5.7 Conclusions

1. ZSM-5, Y, β zeolites and phosphotungstic acid are investigated as catalysts for the ammonolysis of t-butyl alcohol with anhydrous ammonia. The products of the reaction were t-butylamine and isobutene.
2. It is observed that the variation of Si/Al ratio of HZSM-5 zeolite has a pronounced effect on the catalytic activity. For the three different HZSM-5 zeolite viz. HZSM-5(40), HZSM-5(80) and HZSM-5(225) the catalytic activity followed the order HZSM-5(40) > HZSM-5(80) > HZSM-5(225).
3. Y and β zeolites showed a very low activity for the formation of amines.
4. NiZSM-5 zeolite was found to be the most active catalyst for the synthesis of t-butylamine. Highest conversion of alcohol to amines (~30 %) was obtained at a temperature of 320 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 3.
5. HPWA gave a high dehydration activity and exhibited a poor selectivity towards formation of t-butylamine.
6. Modification of NiZSM-5 with HPWA lowered the catalytic activity.
7. The catalytic activity was found to increase with Ni content of NiZSM-5 zeolite.
8. The presence of water in the feed resulted in lowering the selectivity towards t-butylamine.
9. Bronsted acid sites are responsible for the dehydration of the alcohol and weak acid sites are believed to be the active sites for the ammonolysis

reaction. The formation of t-butylamine takes place via intermolecular dehydration of t-butyl alcohol and ammonia.

10. HZSM-5(40) zeolite was found to be the most active catalyst for the ammonolysis reaction of t-butyl alcohol with aqueous ammonia

Chapter 6

Summary and conclusions

Summary and conclusions

This Chapter summarises the contents of the thesis and also highlights the main conclusions. The scope for future work in this area is also described.

Chapter 1. Introduction and Literature Survey

This Chapter introduces various aspects of ammonolysis, reviews the literature on ammonolysis and also describes the catalytic systems used in this investigation.

Ammonolysis is the cleavage of a bond by addition of ammonia. A wide variety of inorganic and organic substrates can be ammonolysed. Aliphatic amines are of considerable importance and find applications in almost every field of modern technology, agriculture and medicine. There are various methods for the synthesis of amines but ammonolysis of alcohols is the most popular method. The ammonolysis reaction is extensively studied for methyl alcohol and ethyl alcohol, however reports on butyl alcohols very few. Also the reported yields for sec- and t- butyl alcohols are low. Catalysts used for ammonolysis of various alcohols have been listed in this chapter.

Zeolites and heteropoly acids are being extensively used in various catalytic applications owing to their acidic properties. The structure, properties and applications of these classes of compounds in catalysis have been described in this chapter.

Chapter 2. Experimental

This Chapter describes the preparation and the characterisation of the catalysts used in this investigation. The preparation of various catalysts is described. The catalysts are characterized by X ray diffraction, infrared spectroscopy and BET surface area measurements. Temperature programmed desorption using ammonia and carbon dioxide as probe molecules has been carried out over the catalysts to evaluate the acid and basic sites of the catalyst respectively.

Main conclusions

- X ray studies revealed that HPWA interacts strongly with zeolite supports in case of both HZSM-5(225) as well as HY zeolite as evident from the additional absorption peaks which are not present in the pure catalysts.
- In the composite catalysts of HPWA and HY, the Keggin structure bands of HPWA grow in intensity as the concentration of HPWA increases from 10 % to 40 % indicating that the bulk properties of HPAs prevail at higher loadings of HPWA on the support.
- For the HPWA/HY composite catalysts of different compositions, the BET surface area decreased progressively with an increase in HPWA content.
- The composite catalysts of HPWA with HY zeolite showed variable acid strengths. The reason for this could be the interaction of HPWA with the support. Owing to this interaction between HPWA and the zeolites additional acid sites may be generated or there may be modification of acid sites present in the pure catalysts.

Chapter 3. Ammonolysis of n-butyl alcohol

This Chapter describes the catalytic activity of various catalysts for the synthesis of amines by the ammonolysis reaction of n-butyl alcohol with ammonia. The ammonolysis reaction of n-butyl alcohol is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia over ZSM-5, Y and β zeolites and phosphotungstic acid. 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 formation of undesirable products. The catalytic activity is correlated to the catalyst characteristics. The products of the reaction were found to be n-butylamine, dibutylamine, tributylamine, butyraldehyde, butyronitrile and 1-butene.

Main conclusions

- It is observed that the variation of Si/Al ratio of HZSM-5 zeolite has a pronounced effect on the catalytic activity. For the three different HZSM-5 zeolite viz. HZSM-5(40), HZSM-5(80) and HZSM-5(225), it is observed that the percentage conversion of alcohol decreases as the Si/Al ratio increases. However, the selectivity towards amines and the molar percentage conversion of alcohol to amines increases with an increase in Si/Al ratio.
- Naβ zeolite was found to be highly active catalyst for the selective synthesis of dibutylamine. Highest conversion of alcohol to amines at high selectivity towards dibutylamine (~ 55 %) was observed at a temperature of 450 °C, LHSV of 0.75 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 3 over Naβ zeolite catalyst. Under the same

conditions of temperature and LHSV but at an alcohol to NH_3 molar ratio of 1 : 6, the selectivity to n-butylamine was ~ 54 %.

- HZSM-5(225) zeolite was found to be the most active catalyst for the synthesis of amines by the reaction of n-butyl alcohol and ammonia among all the zeolite catalysts showing ~ 50 % conversion of alcohol to amines at a temperature of 400 °C, LHSV of 1.25 h^{-1} and alcohol to ammonia molar ratio of 1 : 5.
- Ammonolysis occurs through Eley – Rideal type mechanism wherein the ammonia from gas phase could collide with the adsorbed alcohol to yield the butylamines. TPD of ammonia is useful in elucidating reaction mechanism of ammonolysis reaction.
- Catalysts having very high acidity such as HPWA and HZSM-5(40) which gave a high dehydration activity, exhibited a poor selectivity towards formation of amines.
- The catalyst 20%HPWA/HZSM-5(225) was found to be the most active catalyst and showed a high selectivity towards n-butylamine. Highest conversion of alcohol to amines (~ 73 %) was observed at a temperature of 400 °C, LHSV of 1.00 h^{-1} and molar ratio (alcohol : NH_3) of 1 : 5.
- Relatively strong acid sites favour a high conversion of alcohol to amines as well as high selectivity to amines.

Chapter 4. Ammonolysis of sec-butyl alcohol

This Chapter describes the catalytic activity of various catalysts for the synthesis of sec-butylamines by the ammonolysis reaction of sec-butyl alcohol with ammonia. The ammonolysis reaction of sec-butyl alcohol is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia over ZSM-5, Y and β zeolites and phosphotungstic acid. 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 formation of undesirable products. The catalytic activity is correlated to the catalyst characteristics. The products of the reaction were found to be sec-butylamine, di-sec-butylamine, tri-sec-butylamine, ethyl methyl ketone and 2-butene.

Main conclusions

- HZSM-5(40) zeolite was found to be the most active catalyst for the synthesis of amines by the reaction of sec-butyl alcohol and ammonia among various ZSM-5 zeolites.
- HY zeolite is found to be the most active catalyst for the synthesis of amines by the reaction of sec-butyl alcohol and ammonia among the various Y zeolites.
- Hβ zeolite is found to be an efficient catalyst for the synthesis of sec-butylamine by the ammonolysis reaction of sec-butyl alcohol. The best yields over Hβ zeolite are obtained at a temperature of 400 °C, LHSV of 2.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 5 where in ~ 62 % overall conversion of the alcohol occurs at ~ 80 % selectivity towards amines out of which ~ 65 % is sec-butylamine.

- The composite catalyst 20%HPWA/HY was found to be highly active catalyst for the synthesis on sec-butylamine by ammonolysis of sec-butyl alcohol. The catalyst showed ~ 70 % conversion of alcohol to amines with a high selectivity towards n-butylamine at a temperature of 400 °C, LHSV of 1.00 h^{-1} and an alcohol to ammonia molar ratio of 1 : 6.
- The composite catalyst 30%HPWA/HY was found to be the most active catalyst and showed a high selectivity towards di-sec-butylamine. Highest conversion of alcohol to amines (~ 80 %) was observed at a temperature of 350 °C, LHSV of 0.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 4.
- A higher relative proportion of strong acid sites favoured a high conversion of alcohol to amines.

Chapter 5. Ammonolysis of t-butyl alcohol

This Chapter describes the catalytic activity of various catalysts for the synthesis of amines by the ammonolysis reaction of t-butyl alcohol with anhydrous and aqueous ammonia. The ammonolysis reaction of t-butyl alcohol is investigated as a function of temperature, LHSV and molar ratio of alcohol and ammonia over ZSM-5, Y and β zeolites and phosphotungstic acid. The products of the reaction are found to be t-butylamine and isobutene. The reaction is investigated to find a catalyst that would give selective production of t-butylamine in high yields and at the same time suppress the formation of isobutene. The catalytic activity is correlated to the catalyst characteristics.

Main conclusions

- It is observed that the variation of Si/Al ratio of HZSM-5 zeolite has a pronounced effect on the catalytic activity. For the three different HZSM-5 zeolite viz. HZSM-5(40), HZSM-5(80) and HZSM-5(225) the catalytic activity followed the order HZSM-5(40) > HZSM-5(80) > HZSM-5(225) in the case of anhydrous ammonia as well as aqueous ammonia.
- NiZSM-5 zeolite was found to be the most active catalyst for the synthesis of t-butylamine by the ammonolysis of t-butyl alcohol with anhydrous ammonia. Highest conversion of alcohol to amines (~30 %) was obtained at a temperature of 320 °C, LHSV of 1.50 h^{-1} and an alcohol to ammonia molar ratio of 1 : 3. The catalytic activity was found to increase with Ni content of NiZSM-5 zeolite.
- The presence of water in the feed resulted in lowering the selectivity towards t-butylamine.

- Bronsted acid sites are responsible for the dehydration of the alcohol and low temperature acid sites i. e. weak acid sites may be the active sites for the ammonolysis reaction. The formation of t-butylamine takes place via intermolecular dehydration of t-butyl alcohol and ammonia.

HZSM-5(40) zeolite was found to be the most active catalyst for the ammonolysis of t-butyl alcohol with aqueous ammonia.

Table 6.1 Summary of important results.

Alcohol	Active Catalysts	Remarks
N-butyl alcohol	Naβ	Selective towards dibutylamine
	20%HPWA/HZSM-5(225)	Most active and selective towards n-butylamine
Sec-butyl alcohol	HZSM-5(40),HY and Hβ	Mixed selectivities towards different amines
	20%HPWA/HY	Highly selective towards sec-butylamine
	30%HPWA/HY	Most active and highly selective towards di-sec-butylamine
T-butyl alcohol	NiZSM-5	Most active catalyst with anhydrous ammonia Catalyst activity depends on Ni content
	HZSM-5(40)	Most active catalyst with aqueous ammonia

6.1 Scope for future work

- Naβ zeolite is found to be an active and highly selective catalyst for the synthesis of dibutylamine by the reaction of n-butyl alcohol and ammonia. The catalytic activity of β zeolite with other basic cations like K, Rb etc. can be studied for the reaction since the activity of the catalyst is favoured by a high total basicity. This could also throw more light on the role of basic sites for the ammonolysis reaction.
- A more detailed investigation of the nature of acid and basic sites of various catalysts can be carried out.
- The effects of temperature, LHSV and molar feed variations have been discussed at various stages in the investigation and some plausible conclusions have been drawn especially with respect to conversion of alcohol and selectivity towards individual amines in a mixture of amines. A generalisation of these conclusions becomes a difficult task because of the side reactions that accompany the main ammonolysis reaction. However kinetic models can be worked out using specific cases and a generalisation of these effects may be proposed. This could have a great significance as very little work has been carried out in this area for the ammonolysis reactions.

The catalytic activity of salts of phosphotungstic acid can be studied for the ammonlysis reactions of the various alcohols and also tailoring of the catalyst may be possible by choosing a salt having a higher proportion of active acid sites that assist the formation of amines from a particular alcohol as desired by the ammonolysis reaction of the particular alcohol. Also these salts could be supported on zeolite catalysts to obtain higher yields and selectivity.

References

References

1. Kirk-Orthmer, Encyclopedia of Chemical Technology, vol. 2, 2nd Ed., Wiley Interscience, (1982).
2. Unit processes in organic synthesis, P.H. Groggins, fifth edition, Tata McGraw-Hill Publishing Company Limited New Delhi, 1995.
3. M. Cotiga and C. Fagarasan, Rom. Patent 19790129 (1981).
4. R. D. Shannon, M. Keane, Jr., L. Abrams, R. H. Staley, T. E. Gier, D. R. Corbin and G. C. Sonnichsen, J. Catal., 113 (1988) 367.
5. N. S. Kozlov and N. I. Panova, Zhurnal Obschei Khimii, 26 (1956) 2602.
6. F. V. Bel'chev and T. Belorussk, Sel'skokhoz. Akad., 27 (1958) 87.
7. Kh. M. Minachev, A. I. Maksimov, I. V. Mishin and I. I. Levitskii, Doklady Akademii Nauk SSSR, 280 (1985) 1154.
8. Kh. I. Areshidze and E. K. Tavartkiladze, Tr. Tbilis. Univ., 4 (1972) 143.
9. L. A. Hamilton, US Patent 3384667 (1968).
10. H. Abe and A. T. Bell, J. Catal., 142 (1993) 430.
11. A. N. Bashkirov, N. S. Zakirov, E. A. Abdurakhmanov, G. A. Kliger, K. Muradov, and Yu. S. Snagovskii, Neftekhimiya, 27 (1987) 818.
12. L. G. Jodra, M. C. M. Palancar and A. R. Salvador, Anales de Quimica, Serie A: Quimica Fisica e Ingenieria Quimica, 79 (1983) 228.
13. N. R. Bukeikhanov, L. V. Li, R. K. Al'mukhambetova, P. B. Vorob'ev, B. T. Dzhusupov, and B. V. Suvorov, Izvestiya Akademii Nauk Kazakhskoi SSSR, Seriya Khimicheskaya, 1(1983) 64.

14. E. Kh. Korchagova, E. Dziluma, V. A. Slavinskaya, and A. Avots, Zhurnal Prikladnoi Khimii, 55 (1982) 2784.

15. L. V. Li, N. R. Bukeikhanov, B. V. Suvorov, P. B. Vorob'ev and R. K. Al'mukhambetova, Izvestiya Akademii Nauk Kazakhskoi SSR Seriya Khimicheskaya, 4 (1982) 54.

16. M. M. Marisic, W. I. Denton and R. B. Bishop, US Patent 2478464 (1949).

17. W. I. Denton and C. J. Planck, US Patents 2540787 - 2540789 (1951).

18. W. I. Denton et. al., Ind. Eng. Chem., 42 (1950) 796.

19. N. Mizuno, M. Tabata, T. Uematsu and M. Iwamoto, J. Catal., 146 (1994) 249.

20. M. Deeba, M. E. Ford and T. A. Johnson, J. Chem. Soc. Chem. Commun., (1987) 562.

21. M. Deeba and M. E. Ford, J. Org. Chem., 53 (1988) 594.

22. N. N. Vorozhtzov and V. A. Kobelev, Compt. Rend. Acad. Sci., 3108 (1934) 111.

23. N. N. Vorozhtzov and V. A. Kobelev, J. Gen. Chem., (1934) 4310.

24. Groggins and Stirton, Ind. Eng. Chem., 28 (1936) 1051.

25. T. J. Deal, F. H. Stross and M. D. Taylor, US Patent 2580284 (1951).

26. A. G. Hill and R. E. Sayre, US Patent 2377233 (1945).

27. P. K. Glasoe, L. D. Scott and L. F. Audrieth, J. Am. Chem. Soc., 63 (1941) 2965.

28. Baltzly, I. M. Berger and A. A. Rothstein, J. Am. Chem. Soc., 72 (1950) 4149.

29. E. M. Arnett, J. G. Miller and A. R. Day, J. Am. Chem. Soc., 72 (1950) 5635.

30. W. P. Ratchford and C. H. Fisher, J. Org. Chem., 15 (1950) 317.

31. E. M. Arnett, J. G. Miller and A. R. Day, J. Am. Chem. Soc., 76 (1951) 5393.

32. A. M. Eastham, B. Darwent and P. F. Beaubein, Can. J. Chem., 29 (1951) 585.

33. G. H. Coleman, Ind. Eng. Chem., 45 (1953) 1915, A. C. Stevenson, Ind. Eng. Chem., 44 (1952) 1983, A. C. Stevenson, Ind. Eng. Chem., 43 (1951) 1920, A. C. Stevenson, Ind. Eng. Chem., 42 (1950) 1664, A. C. Stevenson, Ind. Eng. Chem., 41 (1949) 1846, A. C. Stevenson, Ind. Eng. Chem., 40 (1948) 1584.

34. T. H. Evans and A. N. Bours, Can. J. Technol., 29 (1950) 1.

35. E. C. Hughes et. al., Ind. Eng. Chem., 42 (1950) 7872.

36. E. C. Hughes and F. Veatch, US Patent 2490813 (1949).

37. T. L. Gresham et. al., J. Am. Chem. Soc., 73 (1951) 3168.

38. M. H. Sprung, Chem. Rev., 26 (1940) 297.

39. G. F. Buckley and N. H. Ray, Brit. Patent 622955 (1949).

40. G. S. Myers, US Patent 2571053 (1951).

41. L. J. Dankert and D. A. Permuda, US Patent 2571106 (1951).

42. A. T. Larsen, US Patent 2497310 (1950).

43. J. F. Olin and J. F. McKenna, US Patent 2365721 (1944).

44. R. H. Goshorn, US Patent 2349222 (1944).

45. R. H. Goshorn, US Patent 2389500 (1945).

46. P. Davies, P. W. Reynolds, R. R. Coats and A. W. Taylor, US Patent 2609394 (1952).

47. A. Bogrow, FIAT Final Report (1948) 716.

48. W. K. O'Loughlin, US Patent 2422743 (1947).

49. Brit. Patent 663,294 (1951)

50. R. B. Flint and P. L. Salzbert, US Patent 2016962 (1935).

51. R. B. Flint and P. L. Salzbert, US Patent 2016963 (1935).

52. M. T. Leffler in Organic Reactions, Vol. 1, R. Adams, ed., John Wiley & Sons, Inc., New York, 1942, Chap. 4.

53. P. Baumgarten, US Patent 2102350 (1938).

54. J. F. Bradzil, L. C. Glaeser and M. A. Toft, US Patent 4866024 (1989).

55. G. Centi, D. Pesheva and F. Trifiro, Appl. Catal., 33 (1987) 343.

56. L. C. Glaeser, J. F. Bradzil, and M. A. Toft, US Patent 4835125 (1989).

57. S. Yu Burylin, Z. G. Osipova, I. P. Olen'kova, A. V. Kalinkin and A. V. Pashis, Kinet. Katal. 30 (1989) 494.

58. J. L. Callahan, US Patent 3308151(1967).

59. D. G. Jones, US Patent 3412134 (1968).

60. V. M. Zhyznevskii, E. V. Fedevych and G. S. Karaman, Kataliz i Neftekhimiya, 8 (2001) 36.

61. D. T. Chen, L. Zhang, C. Yi and J. A. Dumesic, J. Catal., 146 (1994) 257.

62. M. C. Ilao, H. Yamamoto and K. Segawa, J. Catal., 161 (1996) 20.

63. I. Mochida, A. Yasutake, H. Fujitsu and K. Takeshita, J. Catal., 82 (1983) 313

64. F. Fettig and U. Dingerdissen, Chem. Eng. Technol., 15 (1992) 202.

65. Ch. Gruendling, G. Eder-Mirth and J. A. Lercher, Res. Chem. Intermediates 23 (1997) 25.

66. D. T. Chen, L. Zhang, J. M. Kobe C. Yi and J. A. Dumesic, J. Mol. Catal., 93 (1994) 337.

67. Ch. Gruendling, G. Eder-Mirth and J. A. Lercher, J. Catal., 160 (1996) 299.

68. L. V. Li, N. R. Bukeikhanov, B. V. Suvorov, R. K. Al'mukhambetova and P. B. Vorob'ev, Izv. Akad. Nauk. Kaz. SSR, Ser-Khim, 4 (1983) 53.

69. A. K. Maketov, B. V. Suvorov and N. R. Bukeikhanov, Vestn. Akad. Nauk. Kaz. SSR, 3 (1988) 53.

70. G. A. Vedage, L. A. Emig, H. Li and J. N. Armor, US Patent 5917092 (1999).

71. M. Irgang, J. Schossig, W. Schroeder and S. Winderl, German Patent 3903367 (1990),

72. L. Feng and Y. Zhang, Faming Zhuanli Shenqing Gongkai Shuomingshu (2002).

73. K. K. Pitale and R. A. Rajadhyaksha, Current Science, 54 (1985) 447.

74. G. O. Kurme, J. Lommen and F. W. Lommen, US Patent 1832534(1931).

75. N. D. Cheronis and K. H. Spitzmueller, J. Org. Chem., 6 (1941) 349.

76. J. F. Olin, US Patent 2278372 (1944).

77. W. I. Denton and R. B. Bishop, US Patent 2450637 (1948).

78. J. W. Teter, US Patents 2381470 - 2381473 (1945).

79. J. W. Teter, US Patent 2397705 (1946).

80. J. W. Teter, US Patents 2417892 - 2417893 (1947).

81. J. G. Thompson, H. J. Krase and K. G. Clark, Ind. Eng. Chem., 25 (1933) 1092.

82. W. F. Gresham, Brit. Pat. 628659 (1949).

83. Mc-Graw Hill Encyclopaedia of Science and Technology, Vol I, Mcgraw - Hill Inc., 1977.

84. D. Max Roundhill, Chem. Rev., 92 (1992) 1.

85. Egly and Smith, Chem. Eng. Prog., 44 (1948) 387.

86. Enyclopaedia of Chemical Processing And Design, J. J. Meketta, Marcel Dekker Inc. 1977.

87. A. Baiker, J. Kijenski, Catal. Rev. Sci. Eng., 27 (1985) 653.

88. V. A. Nekrasova, N. I. Shuikin, Russ. Chem. Rev., 34 (1965) 843.

89. W. Schmidt, H. Albercht, German Patent 611283 (1935).

90. H. R. Arnold, US Patent 2078922 (1937).

91. W. Schrauth, German Patent 611924 (1935).

92. W. Whiteland, British Patent 649980 (1951).

93. Y. Takita, Y. Nishida, T. Seiyama, Bull. Chem. Soc. Jpn. , 49 (1976) 3699.

94. W. W. Kaeding, US Patent 4082805 (1978).

95. W. S. Emerson. Organic Reactions, vol 4, R. Adams (Jr) ed., Wiley, New York, (1948) 174.

96. P. N. Rylander, Catalytic Hydrogenation over Platinum Metals, Academic Press, New York, (1967). 291.

97. G. A. Kliger, L. S. Glebov, R. A. Friedman, L. A. Vytnova and A. N. Bashkirov, Kinet. Katal, 19 (1978) 615.

98. J. J. Ritter, P. P. Minieri, J. Am. Chem. Soc., 70 (1948) 4045.

99. W. Howk, E. L. Little, S. L. Scott, G. M. Whitman, J. Am. Chem. Soc., 76 (1954) 1899.

100. D. Forster, V. W. Weiss, US Patent 3882181 (1975).

101. H. Greenfield, Ind. Eng. Chem. Prod. Res. Dev., 6 (1967) 142.

102. Engelhard Industries Inc., British Patent 925458 (1963).

103. A. Fischer, M. Maciejewski, T. Burgi, T. Mallat and A. Baiker, J. Catal., 183 (1999), 373.

104. G. Jenzer, T. Mallat and A. Baiker, Cat. Lett., 61 (1999) 111.

105. A. Fischer, T. Mallat, and A. Baiker, J. Catal., 182 (1999), 289.

106. A. Fischer, T. Mallat and A. Baiker, Angew. Chem., Intl. Ed., 38 (1999) 351.

107. P. Sabatier and A. Mailhe, Compt. Rend., 148 (1909) 898.

108. H. R. Arnold, US Patent 1799722 (1931).

109. J. Martin and L.C. Swallen, US Patent 1875747 (1932).

110. C. E. Andrews, US Patent 2073671 (1937).

111. C. E. Andrews and R. N. Washburn, US Patent 2095786 (1937).

112. H. R. Arnold, Brit. Patent 526497 (1940).

113. K. Smeykal, US Patent 2043965 (1936).

114. Hydrocarbon Processing, 52 (1973) 115.

115. Hydrocarbon Processing, 52 (1973) 150.

116. S. Serban, Rev. Chim. (Bucharest), 14 (1963) 451.

117. P Herold and K. Smeykal, US Patent 2068132 (1937).

118. L.C. Swallen and J. Martin, US Patent 1926691 (1933).

119. D. R. Corbin, S. Schwarz and G. C. Sonnichsen, Catal. Today, 37 (1997) 71.

120. J. D. Leonard, Netherlands Application 6607964 (1965).

121. A. B. Brown and E. Reid, J. Phys. Chem., 28 (1924) 1067.

122. H. Heinemann, R. W. Wert and W. McCarter, Ind. Eng. Chem., 41 (1949) 2928.

123. M. A. Popov and N. I. Shuikin, Izv. Akad. Nauk. SSSR, Otd. Khim. Nauk, (1955) 308.

124. F. V. Bel'chev and Tr. Belorussk, Sel'skokhozyaistvennoi. Akad., 31 (1959) 83.

125. E. Gruyot and M. Fournier, C. R. Acad. Sci., 189 (1929) 927.

126. E. Schwoelger and H. Adkins, J. Am. Chem. Soc., 61 (1939) 3499.

127. J. Pasek et. al., Chem. Prum., 21 (1971) 491.

128. I. M. Kolesnikov, V. I. Kovelenko, T. I. Kovelenko and G. P. Malook, Zh. Fiz. Khim., 46 (1972) 527.

129. V. I. Kovelenko, N. M. Kolesnikov, T. I. Kovelenko and G. P. Malook, Zh. Fiz. Khim., 47 (4) (1973), 1040.

130. L. J. Spillane and R. C. Tallman US Patent 2543424 (1951).

131. M. Chandrakala, R. Ramchandra Rao, S. J. Kulkarni, M. Subrahmanyam and K. V. Raghavan, Indian Journal of Chemistry, 37 (1998) 323.

132. S. P. Naik and J. B. Fernandes, Appl. Catal., 205 (2001) 195.

133. N. S. Kozlov and L. Akhmetshima, Doklady Akad. Nauk SSSR, 85 (1952) 91.

134. B. Yu. Kagan et. al., Neftekhimiya, 7 (1967) 619.

135. G. A. Kliger et. al., Neftekhimiya, 9 (1969) 433.

136. British Patent 1,074,603 (1967).

137. V. A. Bassilli and A. Baiker, Appl. Catal., 65 (1990) 293.

138. Y. Shinohara, T. Yamazaki, A. Niiyama and T. Ono, Japanese Patent 71 23052.

139. Y. Shinohara, T. Yamazaki, A. Niiyama and T. Ono, Japanese Patent 71 23053.

140. G. A. Kliger et. al., Neftekhimiya, 6 (1966) 769.

141. F. H. Van Munster, US Patent 3,351,661 (1967).

142. M. A. Popov, Zhurnal Obshchei Khimii 18 (1948) 1109.

143. V. V. Belov et. al., Neftekhimiya 31 (1991) 642.

144. E. C. Novella, E. R. Jorda and E. L. Morales, Anales de Quimica, Serie A: Quimica Fisica e Ingenieria Quimica, 77 (1981) 283.

145. Y. Meng, Z. Xu, L. Chen, Y. Li and F. Dong, Huaxue Gongye Yu Gongcheng, 15 (1998) 44.

146. S. Gobolus, M. Hegedus, E. Talas and J. L Margitfalvi, Stud. Surf. Sci. Catal., 108 (1997), 131.

147. Y. Cheng, S. Guo and A. Cheng, Gaodeng Xuexiao Huaxue Xuebao, 15 (1994) 760.

148. Y. Hara, H. Kanezaki and M. Takahashi, Japanese Patent JP 07185348 (1995).

149. P. S. Nemphos and D. Hearn, U S Patent 621451 (1995).

150. I. G. Farben Industries, Brit Patent 435200 (1935).

151. L. C. Swallen and J. Martin, Ger. Patent 609245 (1935).

152. Paul Harold, US Patent 206813 (1937).

153. E. B. Punnet, US Patent 2113241 (1938).

154. Elidu Pont de Nemours and Co., Brit. Patent 528987 (1948).

155. F. E. Smith, US Patent2446599 (1948).

156. H. Inmfued and R. Klaus, Ger. Patent 134518 (1979).

157. W. W. Kaeding, US Patent 4082805 (1978).

158. A. J. Tompsett, Eur. Patent 76034 (1983).

159. G. Parker and A. J. Tompsett, GB Patent 20193948 (1982).

160. J. Weigert, US Patent 4313003 (1982).

161. I. Mochida, Jap. Patent, 49340 (1983).

162. M. Deeba and R. N. Cochran, Eur. Patent 85408 (1983).

163. R. N. Cochran and M. Deeba, US Patent 4398041 (1983).

164. J. Tompsett and T. V. Whittam, Eur. Patent 107457 (1984).

165. J. Tompsett, US Patent 4436938 (1984).

166. Y. Ashina, T. Fujita, M. Fukatysu and J. Yagi, Eur. Patent 125616 (1984).

167. M. Deeba, W. J. Ambs and R. N. Cochran, US Patent 4434300 (1984).

168. Kohichi Segawa and Hiroyasu Tachibana, J. Catal., 131 (1991) 482.

169. B. Cheminal, P. Kiener and A. Travesaz, European Patent, 24225 (1981).

170. D. C. Best, US Patent 3278598 (1986).

171. A. Gardner and R. T. Clark, US Patent 4255357 (1981).

172. Air Products and Chemicals Inc., Japanese Kokai 81108744 (1981).

173. J. P. Shen, J. Ma, D. Z. Jiang and E. Z. Min, Catal. Lett., 26 (1994)291.

174. M. Deeba, Eur. Patent 180983 (1985).

175. J. Pasek, J. Marek, K. Bancir and J. Lubojack, Czechoslavakian Patent 185962 (1980).

176. K. Adam and E. Harrer, French Patent 1583299 (1967).

177. B. M. Naasz, I. Boszormenyi and G. A. Somorjai, J. Catal., 115 (1989) 399.

178. H. Abe, H. Taniguchi, K.Okabe, K. Sotoya, Yukagaku, 38 (1989) 565.

179. W.Feng, Z. Yan and Z. Jiang, Riyong Huaxue Gongye, 5 (1989) 211.

180. A. N. Bashkirov, N. S. Zakirov, E. A. Abdurakhmanov, G. A. Kliger, K. Muradov and Yu. S. Snagovskii, Neftekhimiya, 27 (1987) 818.

181. Y. Yokota, I. Hashiba, T. Kawakami and H. Taniguchi, Jpn. Kokai Tokkyo Koho 62149646 (1987).

182. E. Kh. Korchagova, E. Dziluma, V. A. Slavinskaya and A. Avots, Zhurnal Prikladnoi Khimii, 55 (1982) 2784.

183. E. Kh. Korchagova, E. Dziluma, V. A. Slavinskaya and A. Avots, 19790109 (1981).

184. Ajit Kache, H. Rao, P. S. Ramachandran, B. M. Rao and N. M. Reddy, Indian Chemical Manufacturer, 18 (1980) 1.

185. E.C. Habermann, US Patent 4152353 (1979).

186. D. C. Best, Ger. Patent 2700339 (1977).

187. P.Tan and Q. Li, Jingxi Shiyou Huagong, 1 (2004) 11.

188. M. Suzuki and S. Yamamoto, Jpn. Kokai Tokkyo Koho 2004043319 (2004).

189. S. D. Jackson, J. R. Jones, A. P. Sharratt, L. F. Gladden, R. J. Cross and G. Webb, Catalysis of Organic Reactions, 89 (2003) 453.

190. G. Meyer, F. Funke, G. Schulz, D. Kratz, M. Walter and M. Hesse, Ger. Patent 9859776 (2000).

191. T. Hidaka, K. Higuchi, N. Kioke and Y. Miki, Eur. Patent 967011 (1999).

192. K. Nagareda, Y. Tokuda and S. Suzuki, Eur. Patent. 108729 (1998).

193. X. Mao and X. Chen, Zhejiang Daxue Xuebao, Gongxueban 37 (2003) 307-309.

194. W. Wu, B. Sun, J. Ruan, S. Zhang and E. Wang, Faming Zhuanli Shenqing Gongkai Shuomingshu (2001).

195. Jpn. Kokai Tokkyo Koho 58174348 (1983).

196. L. H. Slaugh, US Patent 4206150 (1980).

197. R. A. Fridman, G. A. Kliger, E. I. Bogolepova, Yu. V. Maksimov and I. P. Suzdalev, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya 4 (1976) 744.

198. Y. Hara, H. Kanezaki and M. Takahashi, Jpn. Kokai Tokkyo Koho 07185346 (1995).

199. L. H. Slaugh, Ger. Patent 2749066(1978).

200. P. B. Weisz, V. G. Frillette, R. W. Maatman and E. B. Mower, J. Catal., 1 (1962) 307.

201. C. J. Plank, E. J. Rosinki and M. P. Howthorne, Ind. Eng. Chem. Prod. Res. Dev., 3 (1964) 165.

202. B. P. Venuto and E. T. Habib, Jr., Chemical Industries, Vol. I, Marcel Dekker, New York (1979).

203. W. Holderich and E. Gallei, Chem Ing. Tech., 56 (1984) 908.

204. K. Hedden and J. Weitkamp, Chem Ing Tech, 52 (1980) 99.

205. R. J. Argauer and G. R. Landolt, US Patent 3702886 (1967).

206. T. E. Whyte and R. A. Dallas, Catal. Rev. Sci. Eng., 24 (1982) 567.

207. G. T. Kokotailo and W. M. Meiser, Spec. Publ. Chem. Soc., 33 (1980) 133.

208. P. B. Weisz, Pure Appl. Chem., 52 (1980) 209.

209. N. Y. Chen, J. Maziuk, A. B. Schwartz and P. B. Weisz, Oil Gas J., 66 (1968) 144.

210. N. Y. Chen, R. L. Gorring, H. R. Ireland and T. R. Stein, Oil Gas J., 75 (1977) 165.

211. W. E. Garwood, ACS Symp. Ser. 218 (1981) 383.

212. S. C. Meisel, J. P. Mc Cullough, C. J. Lechthaler and P. B. Weisz, Chem Tech., 6 (1987) 86.

213. A. W. Chester and F. Young, US Patent 4350835(1982).

214. W. Hoelderich, Y. Murakami, A. Lijima and J. W. Ward, Pure Appl. Chem., 58 (1986) 1383.

215. M. Thielen, M. Geelen and P. A. Jacobs, Proc. Zeocat Symp., Siofok (Hungary) (1985).

216. D. W. Breck, Zeolite Molecular Sieves, Wiley Pub., New York (1974).

217. R. M. Barrer, Hydrothermal Chemistry of Zeolites, Axademic Press, New York (1982).

218. W. M. Meier and D. H. Olson, Atlas of Zeolitic Structure Types, 2nd Ed. (1987).

219. W. L. Bragg, The Atomic Structure Minerals, Cornell University Press, New York (1937).

220. W. M. Meier, Molecular Sieves, Soc. Chem. Ind., London (1968).

221. L. B. Sand, Eco. Geol., (1967) 191.

222. E. M. Flanigen, Proc. Of 5th Int. Zeolite Conf., Ed. L. V. C. Rees, Heydon London (1980) 760.

223. M. E. Davis, C. Saldarriage, C. Montes, J. Graces and C. Crowder, Nature, 331 (1988) 968.

224. M. Estermann, L. B. Mecusker, Ch. Bacrlocher, A. Morrouche and H. Kessler, Nature, 352 (1991) 320.

225. E. G. Deroune, E. W. Valyoisik, and A. Von Ballmoos, E. Pat. Appl. 146384 (1984).

226. L. B. Sand, Pure Appl. Chem., 52 (1980) 2105.

227. P. A. Jacobs and J. A. Martens, Synthesis of High Silica Zeolites, Elsevier, (1987) 102.

228. E. P. Parry, J. Catal., 2 (1963) 371.

229. E. G. Derounae, S. Detremmerie and Z. Gabelica, N. Blom, Appl. Catal., (1981) 201.

230. D. W. Breck, Zeolite Molecular Sieves, Wiley, New York (1974).

231. P. B. Weisz and V. J. Frilette, J. Phys. Chem., 64 (1960) 382.

232. T. Okuhara, N. Mizuno and M. Misono, Adv. Catal., 41 (1996) 113.

233. M. Misono, Proc. 10th Int. Congr. Catal., Budapest, 1992; Elsevier: Amsterdam, (1993) 69.

234. M. Misono, Future Opportunities in Catalytic and Engineering Technology, (1990).

235. M. Misono, Proc. Climax 4th Intern. Conf. Chem. Uses Molybdenum, (1982) 289.

236. M. Misono, Catal. Rev. Sci. Eng., 29 (1987) 269.

237. Y.Ono, In Perspectives in Catalysis; Thomas, J. M., Zamaraev, K. I., Eds. Blackwell, London, (1992) 341.

238. I. V. Kozhevnikov and K. I Matveev, Appl. Catal., 5 (1983) 135.

239. Y. Izumi, K. Urabe, and A. Onaka, In Zeolite, Clay, and Heteropolyacids in Organic Reactions; Kodansha: Tokyo; VCH: Weinheim, 1992.

240. I. V. Kozhevnikov, Catal. Rev. Sci. Eng., 37 (1995) 311.

241. Y. Izumi, Catal. Today, 33 (1997) 371.

242. A. Corma, Chem. Rev., 95 (1995) 559.

243. M. Misono, and N. Nojiri, Appl. Catal., 64 (1990) 1.

244. G. A. Tsigdinos, Top. Curr. Chem., 76 (1978) 1.

245. V. F. Chuvaev, K. I. Popov and V. I. Spitsyn, Dokl. Akad. Nauk SSSR, 255 (1980) 892.

246. M. Fournier, C. F-Jantou, C. Rabia, G. Hervé, and S. J. Launay, Mater. Chem., 2 (1992) 971.

247. V. M. Bondareva, T. V. Sandrushkevich, R. I. Maksimovskaya, L. M. Plyasova, A.V. Ziborov, G. S. Litvak and L. G. Detusheva, Kinet. Catal., 35 (1994) 114.

248. M. Misono, N. Mizuno, K. Katamura, A. Kasai, Y. Konishi, K. Sakata, T. Okuhara, and Y. Yoneda, Bull. Chem. Soc. Jpn., 55 (1982) 400.

249. T. Okuhara, S. Tatematsu, K. Y. Lee and M. Misono, Bull. Chem. Soc. Jpn., 62 (1989) 717.

250. L. S. Akaratiwa and H. J. Niiyama, Chem. Eng. Jpn., 23 (1990) 143.

251. M. Furuta, K. Sakata, M. Misono, and Y. Yoneda, Chem. Lett., 1979, 31.

252. G. I. Kapustin, T. R. Brueva, A. L. Klyachko, M. N. Timofeeva, S. M. Kulikov and I.V. Kozhevnikov, Kinet. Katal., 31 (1990) 1017.

253. M. Otake and T. Onoda, Shokubai (Catalysts & Catalysis), 7 (1975) 13.

254. T. Okuhara, T. Nishimura, H. Watanabe and M. Misono, J. Mol. Catal., 74 (1992) 247.

255. M. Misono and T. Okuhara, Chemtech, 23 (1993) 23.

256. R. J. Gillespie, Acc. Chem. Res., 1 (1968) 202.

257. A. Auroux and J. C. Vedrine, Stud. Surf. Sci. Catal., 20 (1985) 311.

258. R. S. Drago, J. A. Dias, and T. O. Maier, J. Am. Chem. Soc., 119 (1997) 7702.

259. W. C. Cheng and N. P. Luthra, J. Catal., 109 (1988) 163.

260. K. Nowinska, R. Fiedorow and J. Adamiec, J. Chem. Soc., Faraday Trans., 87 (1991) 749.

261. K. M. Rao, R. Gobetto, A. Lannibello and A. Zecchina, J. Catal., 119 (1989) 512.

262. J. A. R. van Veer, P. A. J. M. Hendriks, R. R.Andrea, E. J. M. Romers and A. E. Wilson, J. Phys. Chem. 94 (1990) 1831.

263. Y. Izumi and K. Urabe, Chem. Lett., (1981) 663.

264. R. J. J. Jansen, H. M. van Veldhuizen, M. A. Schwegler and H. van Bekkum, Rec. Trav. Chim. Pays-Bas. 113 (1994) 115.

265. M. A. Schwegler, H. van Bekkum and N. A. de Munok, Appl. Catal., 74 (1991) 191.

266. T. Baba, Y. Ono, T. Ishimoto, S. Morikawa and S. Tanooka, Bull. Chem. Soc. Jpn., 58 (1985) 2155.

267. T. Baba, and Y. Ono, Appl. Catal., 22 (1986) 321.

268. V. M. Mastihkin, S. M. Kulikov, A. V. Nosov, I. K. Kozhevnikov, I. L. Mudrakovsky and M. V. Timofeeva, J. Mol. Catal., 60 (1990) 65.

269. F. J. Lefebvre, Chem. Soc., Chem. Commun., (1992) 756.

270. R. Thouvenot, C. Rocchiccioli-Delcheff and M. J. Fournier, Chem. Soc., Chem. Commun., (1991) 1252.

271. R. Thouvenot, M. Fournier and C. J. Rocchiccioli-Delcheff, Chem. Soc., Faraday Trans., 87 (1991) 2829.

272. C. Rocchicioli-Deltcheff, M. Amirouche, and M. Fournier, J. Catal,, 138 (1992) 445.

273. K. Brückman, M. Che, J. Haber and J. M. Tatibouet, Catal. Lett., 25 (1994) 225.

274. C. Rocchiccioli-Deltcheff, M. Amirouche, G. Herve, M. Fournier M. Che and I. M. Tatibouet, J. Catal., 126 (1990) 591.

275. J. M. Tatibouet, M. Che, M. Amirouche, M. Fournier and C. Rocchiccioli-Deltcheff, J. Chem. Soc., Chem. Commun., (1988) 1260.

276. M. Fournier, R. Thouvenot and C. Rocchiccioli-Deltcheff, J. Chem. Soc., Faraday Trans., 87 (1991) 349.

277. M. Fournier, A. Aouissi and C. Rocchiccioli-Deltcheff, J. Chem. Soc., Chem. Commun., (1994) 307.

278. C. Rocchiccioli-Deltcheff, A. Aouissi, S. Launay and M. Fournier, J. Mol. Catal., 114 (1996) 331.

279. S. Kasztelan, E. Payen and J. B. Moffat, J. Catal. 125 (1990) 45.

280. K. Nowinska, R. Fiedorow and J. Adamiec, J. Chem. Soc., Faraday Trans., 87 (1991) 749.

281. I. V. Kozhevnikov, A. Sinnema, R. J. J. Jansen and H. van Bekkum, Catal. Lett., 30 (1995) 241.

282. T. Nishimura, T. Okuhara and M. Misono, Chem. Lett., (1991) 1695.

283. T. Komaya and M. Misono, Chem. Lett., (1983) 1177.

284. C. Rocchiccioli-Deltcheff, A. Aouissi, M. M. Bettahar, S. Launay, and M. Fournier, J. Catal. 164 (1996) 16.

285. M. Misono, Chem. Commun., (2001) 1141.

286. V. V. Balasubramnian, I. S. Kumar, V. Umamaheswari, M. Palanichamy and V. Murugesan, Recent Trends in Catalysis, Narosa Publishing House, (1999) 331.

287. J. M. Newsman, M. J. Treacy, W. T. Koetsier and C. B. de Gruyter, Proc. Royal Soc. London A420 (1998) 375.

288. E. M. Flanigen et. al., Molecular Sieve Zeolites-1 (1971).

289. N. Mizuno and M. Misono, Chem. Rev., 98 (1998) 199.

290. S. B. Kakodkar, S. P. Naik and J. B. Fernandes, Proceedings of Fifteenth National Symposium on Thermal Analysis, 414.

291. S. B. Kakodkar, S. P. Naik and J. B. Fernandes, Bull. Cat. Soc. Ind., 4 (2005) 101.

292. Y. Saito, P. N. Cook, H. Niiyama and E. Echigoya, J. Catal., 95 (1985) 49.

293. T. Okuhara, A. Kasai, N. Hayakawa, M. Misono and Y. Yoneda, Chem. Lett., (1981) 391.

294. S. E. Golunski and D. Jackson, Appl. Catal., 23 (1986) 1.

295. C. N. Satterfield, Heterogenous Catalysis in Practice, McGraw – Hill, London, (1980) 151.

296. R. A. Bayerline, G. B. Mcvicker, L. M. Jaculli and I J. Zilmiak, J. Phys. Chem., 92 (1988) 1667.

ACHIEVEMENT

This thesis is successful in developing highly active catalysts for the synthesis of butylamines by the reaction of butyl alcohols and ammonia.

Sr. No.	**Reactants**	**Desired product**	**Catalyst**
1	n-butyl alcohol and ammonia	n-butylamine	20%HPWA/HZSM-5(225)
2	n-butyl alcohol and ammonia	Dibutylamine	Naβ
3	sec-butyl alcohol and ammonia	sec-butylamine	20%HPWA/HY
4	sec-butyl alcohol and ammonia	di-sec-butylamine	30%HPWA/HY
5	t-butyl alcohol and ammonia	t-butylamine	NiZSM-5

Research Publications

1. **Selective synthesis of dibutylamine over Naβ zeolite catalyst**

   Sachin B. Kakodkar, Sajo P. Naik and Julio B. Fernandes, Bulletin of Catalysis Society of India, 4 (2005) 101-108.

2. **Temperature programmed desorption studies and ammonolysis of n-butyl alcohol over HZSM-5 zeolite catalysts of different Si/Al ratios**

   Sachin B. Kakodkar, Sajo P. Naik and Julio B. Fernandes, Proceedings of Fifteenth National Symposium on Thermal Analysis (2006) 414 –416.

Papers presented in conferences

1. **Ammonolysis of n-butyl alcohol over HZSM-5 zeolite of different Si/Al ratios**

   Sachin B. Kakodkar, Sajo P. Naik, and Julio B. Fernandes, presented at National Workshop on Catalysis held at Loyola College, Chennai, 2004.

2. **Catalytic activity of HZSM-5 zeolites of different Si/Al ratios for the ammonolysis reaction of sec-butyl alcohol**

   Sachin B. Kakodkar, Sajo P. Naik, and Julio B. Fernandes, presented at ISCAS 2005 held at Goa University, Goa, 2005.

3. **Temperature programmed desorption studies and ammonolysis of n-butyl alcohol over HZSM-5 zeolite catalysts of different Si/Al ratios**

   Sachin B. Kakodkar, Sajo P. Naik , and Julio B. Fernandes, presented at Thermans 2006 held at University of Rajastan, Jaipur, 2006.