CHAPTER V

SUMMARY
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Wide pore zeolites are extensively used in petroleum and petrochemical industry. In recent years much work on wide pore zeolites like Y and mordenite in the synthesis of fine chemicals is reported. Zeolite omega is a synthetic counterpart of the mineral mazzite. The aluminosilicate framework consists of columns of gmelinite cages bridged by oxygen atoms to give a 12 membered cylindrical main channel system along the crystallographic c axis with a diameter of 7.4Å. The topology of zeolite omega consists of one dimensional channel structure. The silica alumina ratio of omega zeolite varies from 5-10. The Na form is thermally stable, however, the protons form of Al-omega is stable upto 823 K. Due to the high alumina content and more acidic nature like faujasite with wide pore, omega zeolite is a potential material for catalytic purpose. Hence detailed study was undertaken in the synthesis, modification, characterization and catalytic applications.

Zeolite Al-omega was synthesized hydrothermally using TMAOH (25 wt. % methanol) between temp. range 383 to 413 K. The crystallization kinetics was studied to obtain the apparent activation energies of the nucleation process and crystal growth process. The crystallization kinetics curve at different temperatures show sigmoidal or S shape in nature indicating different rates of crystallization at different times. The curves show that the kinetics of crystallization depends on the temperature. The crystallization was treated as first order reaction as the major part of the crystallization curve is almost linear. Since nucleation is the rate determining step, the activation energy of nucleation is calculated from the Arrhenius equation which expresses the temperature dependance of the rate of nucleation. The value for apparent activation energy of nucleation (En) is 82.9 KJ mol\(^{-1}\) and that of crystallization (Ec) is 65.6 KJ mol\(^{-1}\).
The gallosilicate analog was synthesized with the same oxide mole composition except that gallium nitrate was used in place of sodium aluminate. In order to maintain the sodium content equivalent to that in the sodium aluminate, additional quantity of sodium hydroxide was added during the synthesis. The incorporation of Ga in the omega framework was confirmed by chemical analysis, XRD, framework IR and solid state MAS NMR spectra.

From XRD, the lowering of 20 values for the XRD reflections in Ga-omega as compared to those in Al-omega was observed. The unit cell volume obtained from XRD data for Ga-omega (2225 Å³) was found to be atleast marginally higher than that (2210 Å³) for Al-omega zeolite. The IR spectra of Ga-omega show a lower wavenumber for all the structure-sensitive vibrations, due to incorporation of heavier Ga atoms, as compared to those of Al-omega. The 71Ga MAS NMR spectrum confirms the tetrahedral coordination of Ga³⁺ species in the omega framework. Al-omega exhibited spherical crystallites (3 µm), whereas a cylindrical morphology (3.5 - 8.0 µm) was obtained for Ga-omega. Chemical analysis shows that the sodium occupancy in Ga omega (90%) is higher than that in Al-omega (79%). The sodium form of Al and Ga-omega are stable upto a temperature around 1173 K. Sorption uptakes were found to be higher for Al-omega than for Ga-omega.

XRD profiles and thermo analytical data show that NH₄-Ga-isomorph of omega possesses considerably lower thermal stability. The thermal stability is also enhanced to some extent by La exchange; whereas the protonic forms seems to be responsible for lowering the thermal stability. The protonic form of aluminum is comparatively more stable than that of protonic form of Ga-omega. FTIR spectra in framework region show highly crystalline nature of all synthesized samples. It is also revealed higher thermal stability of Al compared to Ga-omega zeolite. Spectra in hydroxyl stretching region and of chemisorbed pyridine show both Brönsted and Lewis acidity which are stronger in Al-omega than in Ga-omega zeolite. Thus, FTIR spectra clearly shows that Ga cations are occupying in framework position in Ga-omega zeolite. Thermo analytical data revealed two or three different stages of weight loss in TG curves. Both surface area and micropore volume
estimated from low temperature nitrogen sorption increased on proton exchange and decreased in the lanthanum exchange zeolite. The equilibrium sorption uptakes were found to be lower in gallium isomorphs than those in aluminum isomorphs. The type-I ammonia sorption isotherms showed that the hold-up capacity is highest in lanthanum exchange omega followed by protonic form. The ammonia sorption isotherm data were satisfactorily represented by applying Langmuir, BET, Dubinin equations. However, Freundlich and Sips equations showed limited applicability to the ammonia sorption data. Statistical models of Langmuir and Volmer indicated that ammonia sorption in omega zeolite broadly follow localized sorption model with molecule-molecule interaction. The chemical potential for cation exchanged forms are higher than the corresponding sodium forms of zeolites. Na-Al-omega offered the most homogeneous surface for NH3 sorption whereas the other cationic forms showed heterogeneous character of the surface. The proton form of Al-omega showed highest value of isosteric heat (around 72 kJ mol⁻¹) for ammonia sorption. The sequence of isosteric heat follows H-Al-omega > La-Al-omega > La-Ga-omega > H-Ga-omega > Na-Ga-omega > Na-Al-omega.

The catalytic activity of both Al-and Ga-omega zeolites in the alkylation of phenol using methanol and hydroconversion of n-hexane reactions are studied. The alkylation was studied to evaluate the effect of reaction parameters on the product distribution. Temperature around 673 K was optimum for this reaction. Higher temperature increased gaseous products due to methanol reaction whereas at lower temperature phenol conversion was low. More acidic catalysts like protonic Al-omega zeolite and La-Al-omega zeolite indicated only alkylation of the nucleus. There is no para selectivity in the reaction products. o-Cresol is about 60% of the total cresols. m-Cresol is formed by 1) the isomerization of the primary product p-cresol and 2) by the rearrangement of anisole. Usually ratio of O/C alkylation is high. Some of these secondary reactions like meta cresol formation is noticed depending on the experimental conditions. At high methanol to phenol ratio and at high temperatures methyl anisole and xylenols are also observed. The catalyst deactivated in short time. However, the Ga-analog did not show much of the catalytic activity. The sequence of phenol alkylation activity is H-Al-omega > La-Al-omega > Na-Al-omega > H-Ga-omega.
In n-hexane conversion reaction H-Al-omega and H-Ga-omega are sensitive to coke formation and deactivate fast. Impregnation of 0.1 % platinum in both H-Al-omega and H-Ga-omega brings about remarkable change in the product pattern and stability of the zeolite catalysts. The H-Pt-Al-omega shows higher activity than H-Pt-Ga-omega over the entire range of reaction temperature studied. Irrespective of the conversion level both Al- and Ga-omega samples have shown isomerization activities at lower temperature, whereas only Ga-omega shows high isomerization activity even at high temperature. Addition of 2% Ga$_2$O$_3$ in Pt-H-Al-omega sample showed higher activity and stability. The activity sequence for n-hexane conversion reaction is 2% Ga$_2$O$_3$ Pt-H-Al-omega > Pt-H-Al-omega > Pt-H-Ga-omega > H-Al-omega > H-Ga-omega.

In general, from the above studies, it is observed that H-Al-omega is more active than La-Al-omega and H-Ga-omega zeolite, which is in broad agreement with thermal, FTIR, sorption kinetics with different probe molecules and ammonia sorption isotherm analysis.