SUMMARY AND CONCLUSIONS

Structurally, zeolites are framework aluminosilicates composed of infinitely extending network of corner sharing SiO_4 and AlO_4 tetrahedra. Mordenite crystallizes in two different varieties on the basis of pore opening as Small Port (SPM) and Large Port (LPM) and belongs to intermediate-silica family. The perfect prismatic fibers of about 0.03 mm thickness of Na-mordenite having formula Na_8 Al_8 Si_{40} O_{96} .24 H_2O exhibited orthorhombic symmetry with unit cell dimensions of a = 18.13 $\overset{o}{A}$, b = 20.49 $\overset{o}{A}$, C = 7.52 $\overset{o}{A}$. Each $(Al,Si)O_4$ tetrahedron belongs to one or more 5-membered rings in the framework. The main elliptical channels (6.7 X 7.0 $\overset{o}{A}$) run parallel to the c-direction and open into smaller channels (2.9 X 5.7 $\overset{o}{A}$) in b-direction.

The present work deals with the synthesis and characterization of synthetic mordenite zeolites. The objective of the work was to study the influence of various factors such as crystallization temperature and time , gross composition of gel on the mordenite synthesis. An attempt was also made on the direct hydrothermal synthesis of mordenite, with framework SiO_2/Al_2O_3 ratio of higher than 10 with and without the aid of template.

Systematic investigation on hydrothermal synthesis of morde-nite in the temperature range 393-453 K have been discussed. The higher apparent activation energy for nucleation (E_n = 87.5 kJ/mole) than that for crystal growth (E_c = 74.71 kJ/mole) revealed the importance of the former step in hydrothermal crystallization of mordenite type zeolites. The crystallite size (1-20 μm) and crystal morphology have been found to be influ-enced by the reactant mole composition and nature of the source

of raw materials and crystallization temperature. In dilute gels (lower pH) and at comparatively lower crystallization temperatures, the smaller crystallites were formed than those synthesized in concentrated gels (higher pH) and at higher crystallization temperatures. The systematic investigations were made on the crystallization behavior by changing the number of moles of water and the concentration of Na_2O oxide moles in the reaction gel on the crystallization of mordenites. The time required to obtain fully crystalline mordenite decreased considerably from 204 hours for OH^-/H_2O of 1.52×10^{-2} to only 27 hours for OH^-/H_2O of 15.2×10^{-2}. This indicates that higher OH^-/H_2O ratio favour the formation of mordenite.

The Na_2O content also showed pronounced effect on crystallization of the nature and purity of the phases obtained. Crystallization temperature and time were also observed as the important parameters in the formation of mordenite irrespective of the Na_2O oxide mole concentration.

The hydrothermal crystallization carried out in the presence of mixed cations (alkylammonium cation + sodium) yielded more siliceous product than that crystallized in the presence of sodium only. To achieve high silica mordenite, various oxide mole composition using silicon dioxide, sodium silicate as a source of silica and 3.0 moles of TEA-Br were crystallized at various temperatures. The dependance of SAR in mordenite was observed on the pH of the initial gel mixture in lower region. The product yield (synthesis efficiency) was 75 % compared to only 20 - 40 % with small port variety. Synthesis efficiency and

product SiO_2/Al_2O_3 ratio were found to increase in the presence of a template. LPM with SiO_2/Al_2O_3 = 25 was also obtained in the absence of template using sodium silicate as silica source and aluminium sulphate as alumina source.

The physico-chemical characterization was done by using modern sophisticated techniques such as XRD, IR, TG/DTA, SEM, ^{29}Si MASNMR and sorption measurements of different probe molecules such as water, benzene, n-hexane and nitrogen. X-ray diffraction pattern and IR spectra in the framework vibration region revealed structural characteristics. A correlation was observed between the % crystallinity calculated from XRD and IR in the higher region. However, IR crystallinity showed higher values than the XRD crystallinity. Thermo-analytical studies showed the stability of mordenite upto 1273 K. The total weight loss in the temperature range of 273 K to 1273 K was found to vary with the % crystallinity as well as silica to alumina ratio. From the weight loss due to removal of template and the chemical analysis of the sample, it can be concluded that a part of the template cations play a role of charge compensation. Wide variation of crystallite size (1-20 μm) and a variety of crystal morphology (cylindrical, cuboids, spherical and irregular) was observed during the present studies as a influence of different synthesis parameters such as nature of reactants, their oxide mole ratios and the temperature. The enhanced hydrophilicity (determined from water uptake) in progressive crystalline phases indicated stepwise aluminium incorporation during the progressive crystallization process. The nature of alumina source and its unreacted contribution in

different crystallinity samples showed surprising trend in the uptake of benzene and n-hexane.

A linear correlation was observed between the aluminium atoms per unit cell and the peak intensity ratio of [111] / [130] and [241] / [002] planes only in the range of 4.6 to 7.8 Al atoms/unit cell. Further decrease in the aluminium atoms per unit cell was found to deviate from the linearity. Thus x-ray measurements under identical conditions indicated the limitations of the relation between aluminium atoms/unit cell and the peak intensity ratios. Based on the low temperature nitrogen sorption, it was found that BET surface area (651 - 579 m^2,g^{-1}) and microporous void volume (0.247 - 0.219 ml,g^{-1}) decreased in mordenite when the SiO_2/Al_2O_3 ratio was increased from 10.4 to 39.9. Equilibrium sorption uptakes at P/P_o = 0.5 and 298 K for different probe molecules like water, benzene was also found to support this observations. Isotherms of sorption of water in the temperature range 303 - 403 K in different mordenite samples with different SAR yielded useful information on the sorption energetics. The sorption of water satisfactorily represented Dubinin equation, however both Langmuir and BET approaches failed to yield the linear plots for water isotherms. Sips equation however, gave linear plots indicating some complicating factor in sorption of water due to formation of aquo-complexes with the sorption center. Langmuir and Volmer coefficients showed involvement of mobile sorption model with sorbate-sorbate interactions. Chemical affinity for water sorption decreases with the increase in SiO_2/Al_2O_3 ratio in the mordenite.

Isosteric heat of sorption could not correlate with the strength of either basic or acidic centres in the mordenite with the variation in SiO_2/Al_2O_3 ratio in the zeolite. The framework Si/Al ratio was also found to influence the IR spectra pattern not only in intensity of the bands at 820 cm^{-1} but also the positions of the bands normally appears at 560, 640 and 1060 cm^{-1}. ^{29}Si MASNMR study revealed the enhanced intensity of Si(OAl) peak at the cost of Si(1Al) peak intensity with the increase in the Si/Al ratio obtained by decreasing the aluminium atoms instead of increasing Si atoms during the synthesis.

Studies on the conversion of n-hexane over Pt-mordenite results complex nature of the reaction including isomerization, cracking and hydrogenolysis. Selectivity for isomerized product decreased with increase in pressure due to increased hydrogenolysis. It also decreases with increase in temperature due to cracking reaction. However, the increase in the pressure of the reaction was found to decrease the conversion of n-hexane marginally.