Chapter 6

Summary And Conclusions
Chapter-6: Summary and conclusions

The thesis describes the hydrothermal synthesis of silicalite-1 and metallosilicate molecular sieves, various physicochemical characterization and in particular, powder XRD studies at non-ambient conditions. The thermal stability of the metallosilicate molecular sieves is checked in-situ using HTXRD technique. Studies on the negative thermal expansion behavior of silicalite-1 and metallosilicate molecular sieves are investigated by in-situ HTXRD analysis. Kinetics of template decomposition from silicalite-1 framework is also studied with in-situ HTXRD technique and the results are correlated with results obtained from thermogravimetric analysis. Orthorhombic to monoclinic phase transition studies in metallosilicate molecular sieves are carried out using low temperature XRD technique and attempts have been made to locate the Fe and Ti atoms in respective silicalite samples. This chapter present a brief summary of the work described in previous chapters and general conclusions arrived from the work.

Chapter 1 provides a general introduction to the zeolites and MFI type molecular sieves. A brief discussion about the powder X-ray diffraction technique with different geometries and its application for various property studies such as determination of crystallinity, crystallite size, phase analysis qualitatively as well as quantitatively, determination of unit cell parameters and structure determination is given in this chapter. Rietveld refinement technique is outlined in this chapter with its principle and various parameters that can be monitored during the Rietveld analysis and information about GSAS (General Structure Analysis System) software used for Rietveld refinement is described briefly. This chapter also describes the applications of powder X-ray diffraction technique for the characterization of zeolite molecular sieves and summarizes the available literature on it. Different applications viz., isomorphous substitution of ‘T’ atoms by heteroatoms, location of ‘T’ atoms in the framework of zeolites and orientation of organic molecules inside the zeolite channels are outlined. The in-situ powder X-ray diffraction technique used at high temperature and low temperature conditions is discussed. The applications of high temperature powder X-ray diffraction in kinetics of solid-state phase transitions, determination of thermal expansion coefficients and reaction kinetics are described briefly. The applications of LTXRD for the study of materials, which are liquids or gases at room temperature, charge density analyses, phase transitions and thermal expansion coefficients, are outlined. It also elucidates the physical principles of other analytical
techniques used for the characterization of metallosilicate molecular sieves such as UV-vis and MAS-NMR spectroscopy. This Chapter is mainly a review of the literature on the above said topics.

Chapter 2 describes the procedure for the hydrothermal synthesis of metallosilicate molecular sieves with different Si/M (M=Fe, Ti and Zr) ratio in synthesis gel. The characterization of the metallosilicate molecular sieves by different techniques viz., X-ray diffraction, TG-DTA, FTIR, SEM-EDAX, DRUV-vis spectroscopy, $^{29}$Si MAS NMR etc. is described in this chapter. Theory and experimental procedure employed for each technique is discussed in this section. This chapter also describes the Rietveld refinement technique employed to extract the unit cell parameters from the powder XRD patterns collected at room temperature. The expansion in unit cell parameters as a result of isomorphous substitution of Si by Fe, Ti and Zr is discussed in this chapter. Determination of Si/M ratio in the framework, with the experimental and theoretical values of unit cell volume using powder XRD data is also discussed in this chapter. The data from the XRD supports the isomorphous substitutions of Si by Fe, Ti and Zr but some of the portion remain as extraframework or other than tetrahedral coordinated atoms, which is concluded by the results of other spectroscopic techniques.

Chapter 3 describes in-situ high temperature X-ray diffraction (HTXRD) studies on silicalite-1 and metallosilicate molecular sieves (FeS-1, TS-1 and ZrS-1) with MFI structure (Si/M = 50) to study the thermal stability and thermal expansion behavior as a function of temperature in the temperature range 298–1623 K. The structure of silicalite-1 and FeS-1 (monoclinic and orthorhombic phase of silicalite-1 and FeS-1) collapsed at 1173 and 1323 K and transformed to α-cristobalite phase. This transformation is irreversible. The structure of TS-1 and ZrS-1 are stable even upto 1623 K. The thermal behavior of trivalent and tetravalent cations in the MFI framework depends on the role of counter cation present in the former. The sharp negative thermal expansion seen in all the samples is anisotropic, with relative strength of contraction in ‘a’ axis is being greater than ‘b’ and ‘c’ axes in TS-1 and ZrS-1 while contraction is less along ‘a’ axis in FeS-1. Lattice thermal expansion coefficients ($a_v$) in the temperature range 298–1023 K are $-6.75 \times 10^{-6} \text{ K}^{-1}$ for silicalite-1, $-12.91 \times 10^{-6} \text{ K}^{-1}$ for FeS-1, $-16.02 \times 10^{-6} \text{ K}^{-1}$ for TS-1 and $-17.92 \times 10^{-6} \text{ K}^{-1}$ for ZrS-1.
The highest lattice thermal expansion coefficients (a_v) obtained are -11.53 x 10^6 K^{-1} for FeS-1 in the temperature range 298–1173 K, -20.86 x 10^6 K^{-1} for TS-1 and -25.54 x 10^6 K^{-1} for ZrS-1, respectively, in the temperature range 298–1623 K. The strength of contraction increases with increase in framework density in the three metallosilicate molecular sieves studied. Tetravalent cation substituted metallosilicate molecular sieves show very high thermal stability, while trivalent cation substituted samples are structurally/thermally less stable. The results of the thermal stabilities are discussed and compared with the theoretical studies in literature.

Detailed study of the negative thermal expansion behavior of these materials is carried out using Rietveld refinement of HTXRD patterns collected in the temperature range 373-673 K for silicalite-1 sample. The bond angles and bond distances are determined from the Rietveld refinement data to look for any structural changes taking place as a function of temperature. The Si-O bond distances, Si-O-Si bond angles and Si-Si non-bonding distances are calculated from the Rietveld refinement results and proposed the intrinsic NTE mechanism. The Si-O bond distances seem to play no role in the NTE, as there is no change in their distances as a function of temperature. The transverse vibrations of the Si-O-Si bridging oxygen atoms decreases the Si-Si non-bonding distances which causes the contraction in the material as a function of temperature. The observed decrease in Si-Si non-bonding distances with the constituent Si-O bond distances remaining constant, supports the correlation that the transverse vibrations of the bridging oxygen atoms in the structure are responsible for the NTE in this material. The chapter also describes the HTXRD studies carried out on the metallosilicate molecular sieves TS-1, FeS-1 and ZrS-1 of different Si/M ratio. All the samples exhibit negative thermal expansion on heating in the temperature range 373-773 K and the strength of NTE increases with decreasing Si/M ratio.

Chapter 4 describes the non-isothermal reaction kinetics of the template decomposition from the as synthesized silicalite-1 framework which has been carried out using thermogravimetric analysis (TGA) and high temperature powder X-ray diffraction (HTXRD) techniques and are compared for the first time in literature. Template burning (or calcinations) of the as-synthesized material is a key step in the activation of a zeolitic material for its application as a catalyst or as a membrane. HTXRD experiments are carried out at different heating rates such as 1, 3 and 5
°C/min, while TG were measured at 10, 15 and 20 °C/min. The kinetic analysis is carried out using the plots of conversion factors (α) versus temperature. Conversion factor for template decomposition is calculated using two methods viz., % weight loss from the thermogravimetric analysis and changes in the intensities of the Bragg reflections 101/011 and 200/020 in the HTXRD patterns scanned at different temperatures (range 298-823 K). A kinetic analysis based on the % weight loss from the TG data and the intensity change of the low angle peaks in the HTXRD patterns is performed using Kissinger and Flynn–Wall–Ozawa methods. According to the Kissinger method, the slope of the plot of \((\ln(\beta/T_p^2)) \) versus \(1/T_p\) is proportional to \(E_a\), according to the following equation: \(\beta\) is the heating rate, \(R\) is the molar gas constant and \(k\) is the reaction rate constant. The calculated apparent activation energy for template decomposition in air is 129 kJ mol\(^{-1}\) (TG) and 125 kJ mol\(^{-1}\) (HTXRD) using the Kissinger method. The alternative method by Flynn–Wall–Ozawa (where the slope of the plot of \(\ln\beta\) vs. \(1/T\) is proportional to \(E_a\)) is also used to calculate the activation energy using the equation. Apparent activation energy for template decomposition in air is 123 kJ mol\(^{-1}\) (TG) and 124 kJ mol\(^{-1}\) (HTXRD) by Flynn–Wall–Ozawa approach. An advantage of this method is that any changes in the mechanism of the reaction are immediately apparent as variations in the slope for different \(α\). The reaction order is determined by Avarami equation using the method of Kennedy and Clark. Avarami equation is successfully used to fit the kinetic data. The value for reaction order is nearly equal to two for all the heating rates. The reaction order determined using the method of Kennedy and Clark, is close to 2 for both the experimental data (TG and HTXRD), which rule out the diffusion limitation. The apparent activation energy \(E_a\) is determined to be 125 kJ mol\(^{-1}\), which is in good agreement with the results reported in the literature. The second order of template decomposition can be attributed to the fact that TPA\(^+\) is positioned in two different orientations inside the silicalite-1 framework. The second order of template decomposition can be attributed to the fact that TPA\(^+\) is positioned in two different orientations inside the silicalite-1 framework; the so called TPA\(_1\) and TPA\(_2\) having an occupancy of 0.6 and 0.4, respectively. Part of the TPA\(^+\) ion in the sinusoidal channel is in the folded conformation, while extended conformation is present in the straight channel. Hence, there may be different mechanism present for template decomposition in these two physically different environments of the template molecule.
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Thermogravimetric analysis is used extensively in the past to study the decomposition of the template cation, TPA$^+$. The weight loss of a sample as a function of temperature is recorded using thermogravimetric analysis. Over the temperature range from 573 to 823 K, the decomposition of template molecules takes place. The loss in weight corresponds exactly to the TPA$^+$ content of the zeolite, for e.g. four template molecules per unit cell (12% weight loss).

Rietveld analysis has been carried out to look into the structural changes taking place in the framework as a function of temperature. Template removal occurs with a contraction in unit cell dimensions. There is a large contraction in the unit cell volume as the template is removed from the framework and it is attributed to the transverse vibrations of Si-O-Si bridging oxygens as a function of temperature. In addition, the unit cell dimensions approach the same values regardless of heating rate.

Chapter 5 describes the investigation of the phase transition temperature for various TS-1 and FeS-1 samples (concentration of Ti and Fe vary) to determine the effect of Si/M ratio on the phase transition temperature. These metallosilicate molecular sieves show orthorhombic phase in Pnma space group at room temperature whereas at low temperature the structure is transformed to monoclinic symmetry in space group $P2_1/n$. The powder X-ray diffraction patterns were recorded at various temperatures from 298 K to 80 K at regular intervals. The scans in the $2\theta$ range 22 to 26$^\circ$ were monitored for the phase transition from the splitting of 1 3 3 reflection of the orthorhombic symmetry into the −3 1 3 and 3 1 3 reflections of the monoclinic symmetry. Attempts have been made to locate the heteroatoms in the silicalite framework for TS-1 and FeS-1 samples at low temperature (below the room temperature and above the temperature of phase transition) by using the Rietveld refinement technique. The experiment to locate the T atoms in the metallosilicate molecular sieves are extremely challenging due to the low concentration of T atoms. Contribution from the thermal atomic displacement parameters should be necessarily lower and hence XRD patterns at low temperature are collected to locate the ‘T’ atoms. The results of the location of heteroatoms are also discussed and compared with the results in literature.