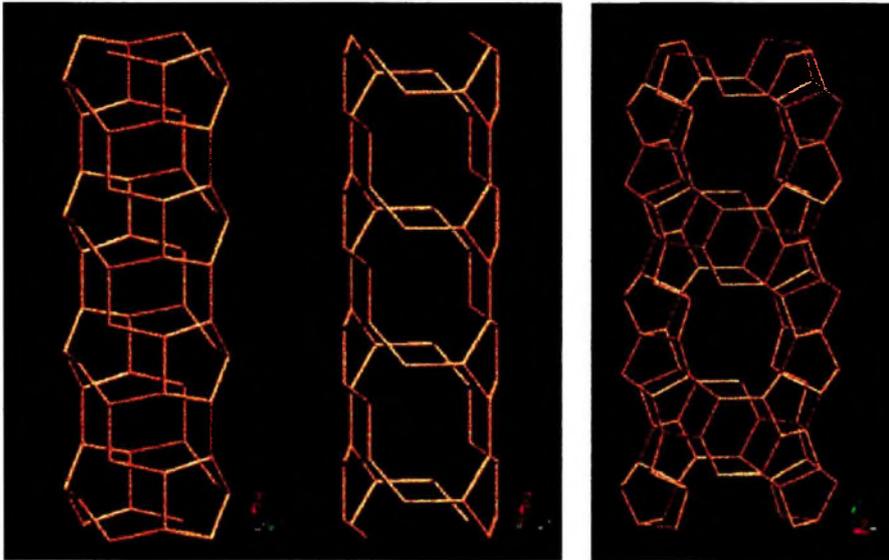


Chapter V



Summary

Summary:

5.1 Introduction:

Ferrierite is a medium pore zeolite belonging to Mordenite group. The ferrierite framework is based on the chains of 5 rings, which are linked to give $[5]^4$ polyhedral units. There are two types of perpendicularly intersecting channels in the structure. The main channels is parallel to the orthorhombic 'c' axis and are outlined by elliptical 10-MR pore with dimension 4.3 x 5.5 Å. The side channels are parallel to the 'b' axis and are outlined by 8-MR pore with dimension 3.4 x 4.8 Å. The silica to alumina ratio of natural ferrierite is around 8 - 10 and is known to be highly siliceous natural zeolite. Ferrierite has been synthesized under hydrothermal conditions using a number of templating species. By varying templates, silica to alumina ratio up to a maximum of 40 could be obtained. Kuperman *et al.* could crystallize pure siliceous form of ferrierite under organothermal synthesis conditions in non-aqueous media. Although a large number of reports and voluminous patent literature is available on ferrierite (FER) system, the detailed characterization and catalytic behavior of various analogs of FER system has not been addressed in the patent literature. Hence, this study was undertaken to better understand and investigate the behavior of Al^{3+} , Fe^{3+} , $Al^{3+} + Fe^{3+}$ and Ti^{4+} species during FER synthesis and their nature in final crystalline product for catalytic applications.

5.2. Synthesis and characterization of Ferrierite:

Zeolite Ferrierite was synthesized hydrothermally mainly using pyrrolidine as template between the temperature range 413-433 K. Sulphuric acid was used to control the pH of the gel. When the sulphuric acid was replaced by equivalent quantities of phosphoric acid or perchloric acid, the crystallization time was reduced. Zeolite Ferrierite crystallized in about 20 h in presence of perchloric acid whereas sulphuric acid required 60h. for crystallization. The crystallized kinetics was studied to obtain the apparent activation energies of nucleation process and crystal growth process. The crystallization kinetic curves at different temperatures (for all the three acids) show sigmoidal or S-shape nature indicating different rates of crystallization depends on temperature as well as type of acid used. The values of Avrami-Erofeev parameters were found to be in accordance with the thermodynamic expectation of decrease in 'k' and increase in 'm' as temperature of Ferrierite synthesis increases. The increase in 'k' and decrease in 'm'

indicate faster nucleation and faster crystallization respectively. The value of apparent energy of activation for nucleation were 42 and 52 KJ/mole and for energy of activation for crystallization were 52 and 60 KJ/mole for perchloric acid and phosphoric acid respectively which, were low than those for sulphuric acid ($E_n = 200$ and $E_c = 163$ KJ/mole) and also in absence of acid ($E_n = 217$ and $E_c = 230$ KJ/mole).

A further interesting information obtained was that optimum amount of aluminum in the gel (~ 0.0008 moles of Al_2O_3) was required for the ferrierite crystallization. In general there no direct relationship was observed between the value of SiO_2/Al_2O_3 of the gel and the final crystalline product. The concentration of aluminum atoms in the ferrierite zeolite is higher than the starting gel. The ferrierite crystallization initially accelerates and stops when most of the aluminum in the gel has been incorporated for framework formation.

Ferrierite was synthesized in presence of tetramethyl ammonium hydroxide as a template and also in the absence of template. In both the cases pure ferrierite could be crystallized with a maximum SiO_2/Al_2O_3 ratio of 21. Samples synthesized by both the methods had similar properties, as the output ratios were nearly same.

Ferrierite was crystallized in reduced amount of pyrrolidine template in presence of an anionic surfactant - sodium bis-(2-ethylhexyl) sulfosuccinate, (AOT) for the first time. 0.02 moles of pyrrolidine were required to crystallize pure ferrierite in presence of AOT as compared to 0.1 moles required for conventional synthesis procedure. Ferrierite could not be crystallized in presence of AOT alone, some minimum amount of pyrrolidine was necessary indicating pyrrolidine is the templating species. It is believed that in presence of AOT, microdroplets are formed. The polar-polar (viz. stern layer of microdroplet) and non-polar non-polar (viz core of microdroplet) interactions between the pyrrolidine and silicate species and / or aluminum species and induce orientation in pyrrolidine molecules. The excess quantity of pyrrolidine required as space filler can be thus avoided due to microdroplet formation. Furthermore, batch to batch particle size distribution was same.

TPD of ammonia, revealed strong acidity for H-FER. Three peaks were observed corresponding to weak medium and strong acid sites. The TPD peak around 823 K is due to Brønsted acid sites. An additional feature is the shift in the TPD peak to the lower temperature as silica to alumina ratio is increased. Furthermore, the α (weak acid site) and β (medium acid site) peaks were found to merge in case of steamed ferrierite.

The ferrisilicate analog of ferrierite was synthesized with the same oxide mole composition except that ferric sulphate was used instead of aluminum sulphate. However, pure ferrierite could not be crystallized from the above gel composition and ZSM-5 co-crystallized along with FER. When 0.1 wt.% H/Al-FER was added as seeds, pure ferrierite crystallized readily. The incorporation of Fe^{3+} in the framework was confirmed by XRD, chemical analysis, framework IR, Mössbauer spectroscopy, UV-vis spectroscopy and ESR spectroscopy.

From XRD, the lowering of 2θ values for XRD reflections in case of Fe-FER as compared to those of Al-FER was observed. The unit cell volume obtained from the XRD data for Fe-FER (1997 \AA^3) was found to be higher than that for Al-FER (1957 \AA^3). The IR spectra of Fe-FER showed an additional band at 650 cm^{-1} indicating Si-O-Fe linkages. Furthermore, the absorption band at 1090 cm^{-1} (asymmetric stretch) shifted to lower frequency for Fe-FER as compared to Al-FER. This shift in the frequency can be explained on the basis of T-O bond distance. Fe-FER samples showed three low intensity peaks around 363, 388 and 417 nm in their UV-vis spectra from which it can be attributed to Fe^{3+} is in tetrahedral environment. ESR spectra of all Fe-FER samples exhibited three signals at around 2.0 and 4.3 corresponding to Fe^{3+} in cationic site location and 4.3 isothermally substituted Fe^{3+} respectively.

Two types iron-substituted ferrierite zeolites of Si/T = 16 ratio were studied by in-situ Mössbauer spectroscopy. Various oxidation and co-ordination states of iron have been identified and their transformations during evacuation and reducing treatment have been monitored.

The Fe-FER exhibited higher stability as for retaining Fe^{3+} ions in T-substituted sites. Upon treatment at 620 K in hydrogen the $\text{Fe}^{3+}_{\text{Td}}$ state was mainly preserved in the Si-O-Fe(OH)-Si groups containing single iron centers. In groups composed from $\text{Fe}_{\text{lattice}}$

O - Fe_{extra-framework} pairs temporary reduction of Fe³⁺_{Td,lattice} to Fe²⁺ state is suggested with one Fe²⁺ component retained still in the framework as confirmed by 77 K Mössbauer spectra. When the framework is stabilized at 300 K later, the redox equilibrium is probably shifted towards the stabilization of Fe³⁺ state in both constituent iron ions.

The Al+Fe-FER sample exhibited a significantly lower stability as for retaining the trivalent ions in T positions. Noticeable amount of Fe³⁺ was reduced to Fe²⁺ state and removal of trivalent ions was also observed upon evacuation. Formation of Al-O-Fe pairs is also suggested. The 650 K treatment in hydrogen results in further irreversible reduction and removal of Fe³⁺_{Td} from the lattice.

With respect to the catalytic ability exhibited only by the Fe-FER zeolite in oxygenation processes, it seems plausible to attribute the catalytic performance to the presence of Fe-O-Fe pairs in which occurrence of redox equilibria was demonstrated.

Pure silicalite with FER topology was synthesized by standardizing the procedure available in the literature. Titanium ferrierite was synthesized by following the procedure for silicalite. However, seeds were found to be mandatory for Ferrierite synthesis. The synthesis temperature ranged in between 160 to 170 ° C for about 5 days. XRD, chemical analysis, UV-vis spectroscopy and framework IR confirmed incorporation of titanium in the framework. Incorporation of titanium in the tetrahedral coordination lead to unit cell expansion of around 30 Å³. Diffuse reflectance UV-vis spectra of TS-FER showed a absorption at 212 nm corresponding to presence of titanium in the framework. Framework region IR for TS-FER showed an additional band at 960 cm⁻¹ further supporting the presence of titanium in tetrahedral environment.

Thermal analysis data for all the samples indicated good stability for ferrierite zeolite and is not dependent on the synthesis route.

5.3. Catalysis on Ferrierite:

The catalytic activity of Al-FER and Fe-FER zeolites in acid catalyzed reactions like isomerization of meta-xylene and alkylation of toluene with methanol are studied. Further, TS-FER and Fe-FER were tested for their activity in epoxidation and hydroxylation reactions respectively.

Catalytic activity of Al-FER and Fe-FER was evaluated in two reactions viz. isomerization of meta xylene and toluene methylation. In these reactions, para xylene, an

industrially important chemical is the product of interest. The influence of temperature, WHSV on the product distribution and para xylene selectivity has been studied.

Al-FER and Fe-FER were found to be active for metaxylene isomerization. For meta-xylene isomerization, the conversion in case of Al-FER was found to low as compared to H-ZSM-5, as the diffusion of the reactant is restricted to the 10 MR pore only. The para selectivity was higher as compared to ZSM-5. H-FER in its un-modified form was less stable and deactivated with time on stream. However, on modification by steaming or by Pt impregnation, its life span increased. Ferrisilicate analog of ferrierite showed lower conversion as compared to H-FER, but the para selectivity was higher. Titanisilicate showed no activity for m-xylene isomerization (~ 3% conversion) indicating very low acidity. Ferrierite synthesized under different synthesis conditions (viz. in AOT, in presence of perchloric acid, etc.) showed excellent para-selectivity (except for non-templated synthesis where the silica to alumina ratio was low ortho to para ratio was one). From the kinetic studies the energy of activation for m- xylene isomerization was 14.5 Kcal. Isofeed studies on two feeds were carried out (viz. lower ethylbenzene concentration and higher ethylbenzene concentration).

Toluene methylation on ferrierite also showed lower conversion but excellent para selectivity (68 - 80%). The conversion could be increased by dealumination. However, catalyst synthesized in perchloric acid media exhibited maximum conversion (42 %). In the case of Fe-FER (ferrisilicate analog of ferrierite) the conversion was higher, but selectivity was low (due to surface reaction). With increase in temperature the conversion increased linearly, however, there was loss of methanol and para selectivity decreased. With increase in WHSV, the conversion decreased but para selectivity was higher. Effect of toluene to methanol mole ratio was also studied and the conversion increased with increase in mole ratio.

Titanium ferrierite (TS-FER) was found to be active in oxidation reactions requiring severe reaction conditions. Two substrates were selected allyl alcohol and styrene. In both the cases, solvent (acetone) played an important role. At higher solvent to substrate ratios the selectivities for respective epoxides were high. Selectivity in case of methanol as solvent was low, due to alcoholysis. Mechanism for titanium ferrierite was postulated to be similar to that of TS-1.

Activity of ferrisilicate analog of ferrierite was tested on mild oxidation reactions like hydroxylation. Fe-FER was active for hydroxylation reaction using hydrogen peroxide as oxidizing agent. Two substrates were examined viz: phenol and benzene. Conversion was found to be higher for phenol. Catechol to hydroquinone ratio was around 1.4. Higher selectivity for catechol may be due to surface reaction. Benzene hydroxylation yielded phenol as the only product however the conversion levels were lower. In all the reactions, H_2O_2 selectivity was low.

In general in this study, ferrierite in its pure form and its ferrisilicate and titanosilicate analogs have been synthesized successfully. Ferrierite has been found to be active in acid catalyzed reactions. It exhibits excellent para selectivity. TS-FER and Fe-FER were also active in oxidation reactions.