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M. Sc. Inorganic Chemistry III Semester
Applied Inorganic Chemistry Lect : 3

Characterization of Zeolite

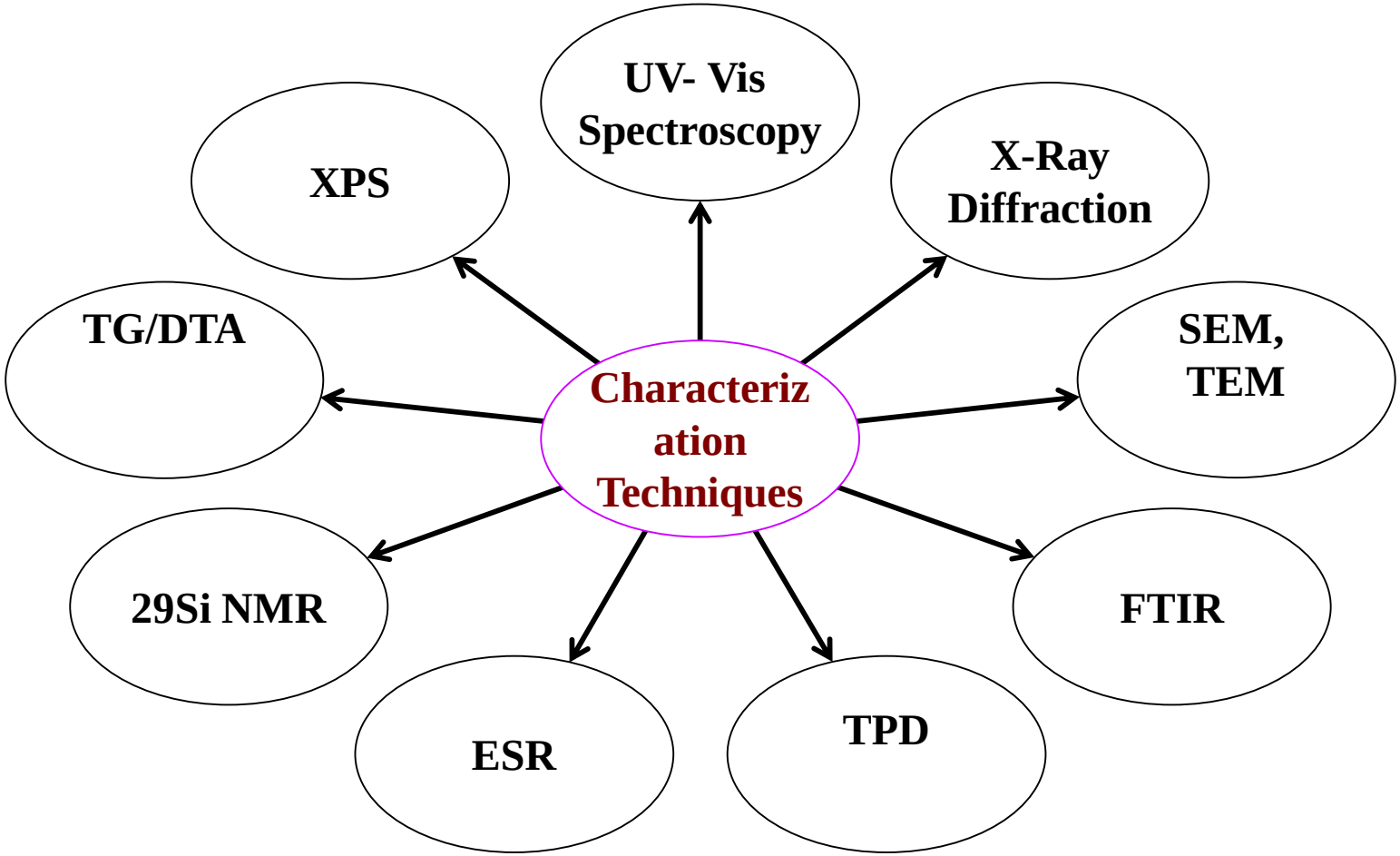
Purpose of characterization of zeolite :

To identify :

- **Active centers on the surface of the catalyst**
- **Morphology**
- **Particle size**
- **Electronic environment**
- **Strength of Lewis & Bronsted acidity**
- **Pore & channel size of zeolite materials**
- **Thermal Stability**

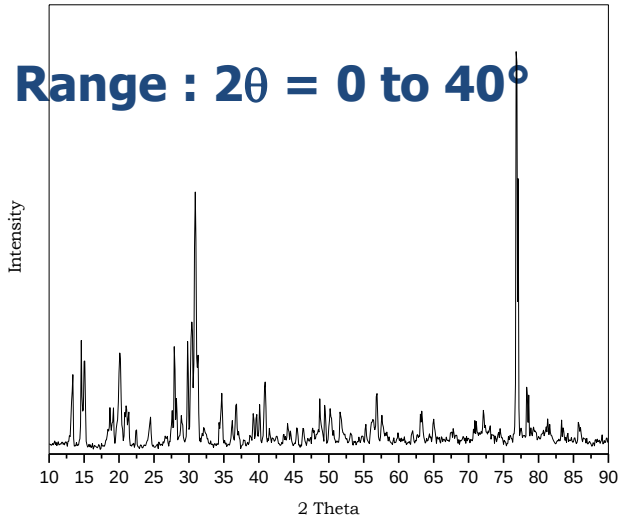
To understand this properties, there is need to characterize the zeolites using suitable sophisticated instrumental techniques

Essential characterization techniques for zeolites

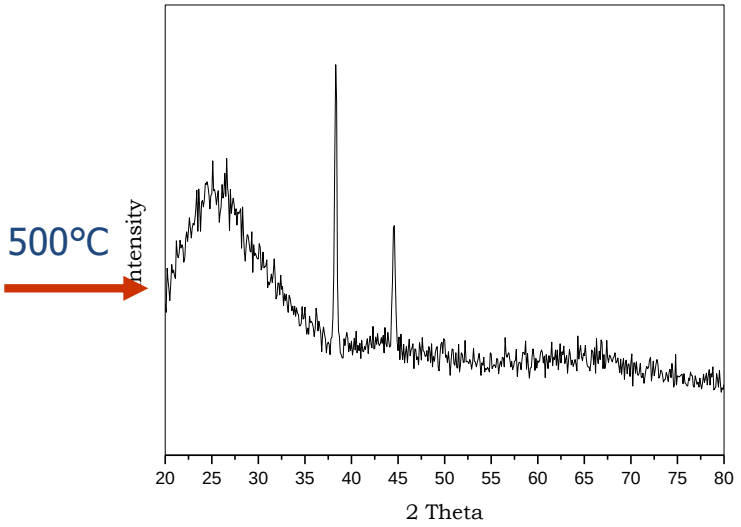


1. Effect of calcinations temperature on natural scolecite zeolite

Natural Scolecite —500°C→ Natural Scolecite after calcination



500°C



high Intense peak at

2θ (°) = 14.90, 20.19, 27.94, 30.83, 76.89

a = 4.817, b = 4.817, c = 34.118

Structure is Hexagonal

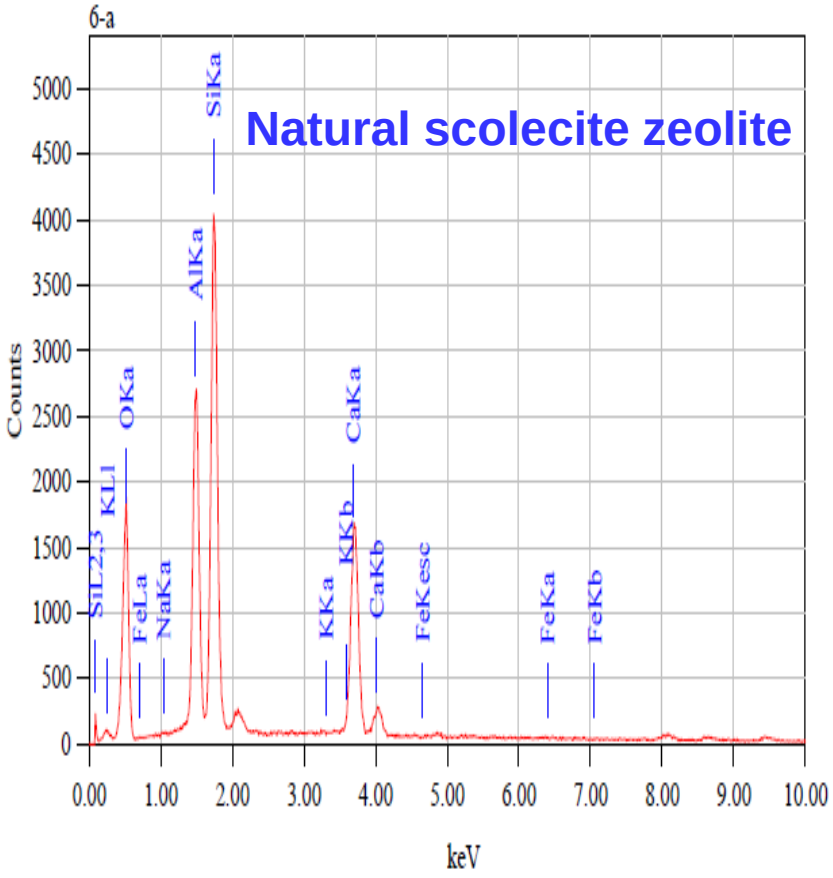
Intense peak at 2θ = 38.29, 44.81°

Broad hump at 2θ = 25-35°

Particle size = 1.9915A °

Hump is due to collapse of interlayer of zeolite.

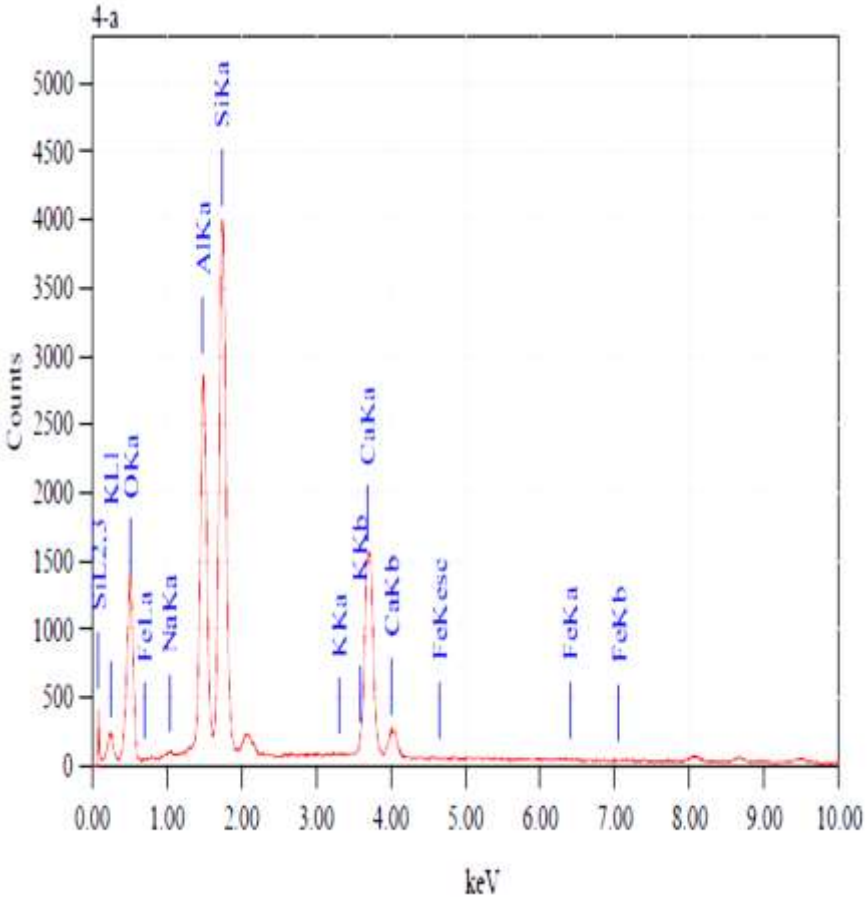
Composition Analysis by EDS



Constituents	Mass (%)	Atom (%)
Si	21.65	16.03
Al	13.41	10.34
Fe	0.09	0.03
Na	0.22	0.20
Ca	13.59	7.05
K	–	–
O	51.03	66.34
Total	100.00	100.00

Si/Al ratio = 1.65

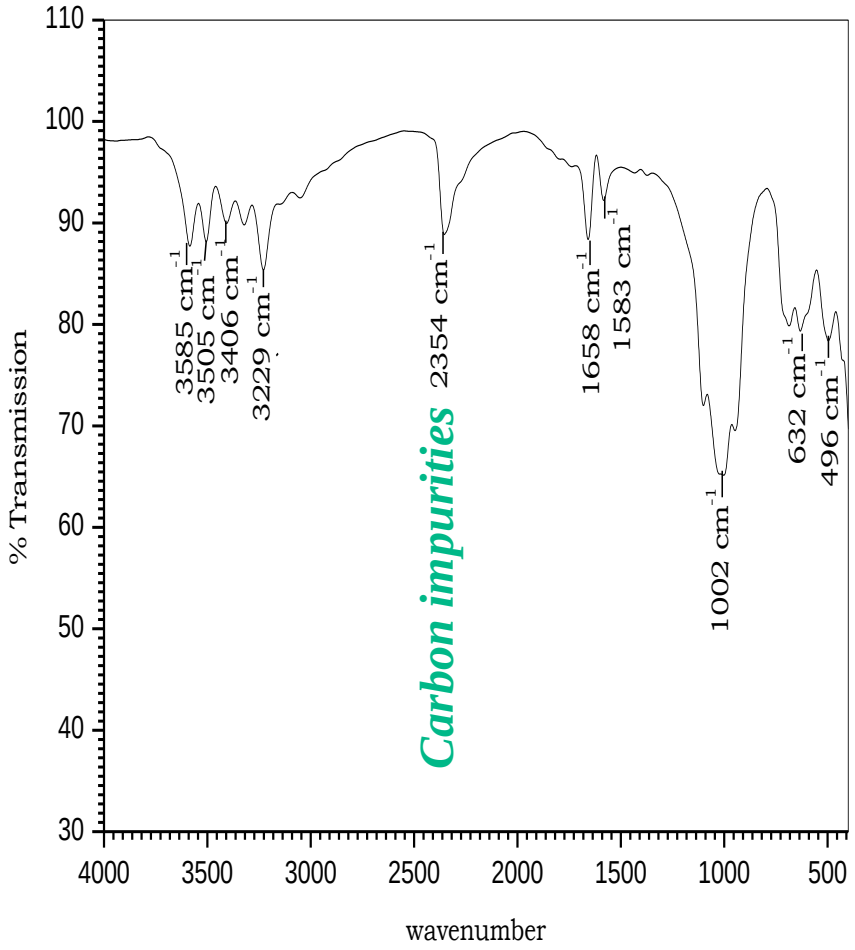
EDS analysis of thermally modified scolecite zeolite



Name of elements	Mass (%)	Atom (%)
Si	23.82	18.17
Al	15.11	12.00
Fe	0.02	0.01
Na	0.28	0.26
Ca	14.70	7.86
K	-	-
O	46.08	61.71
Total	100.00	100.00

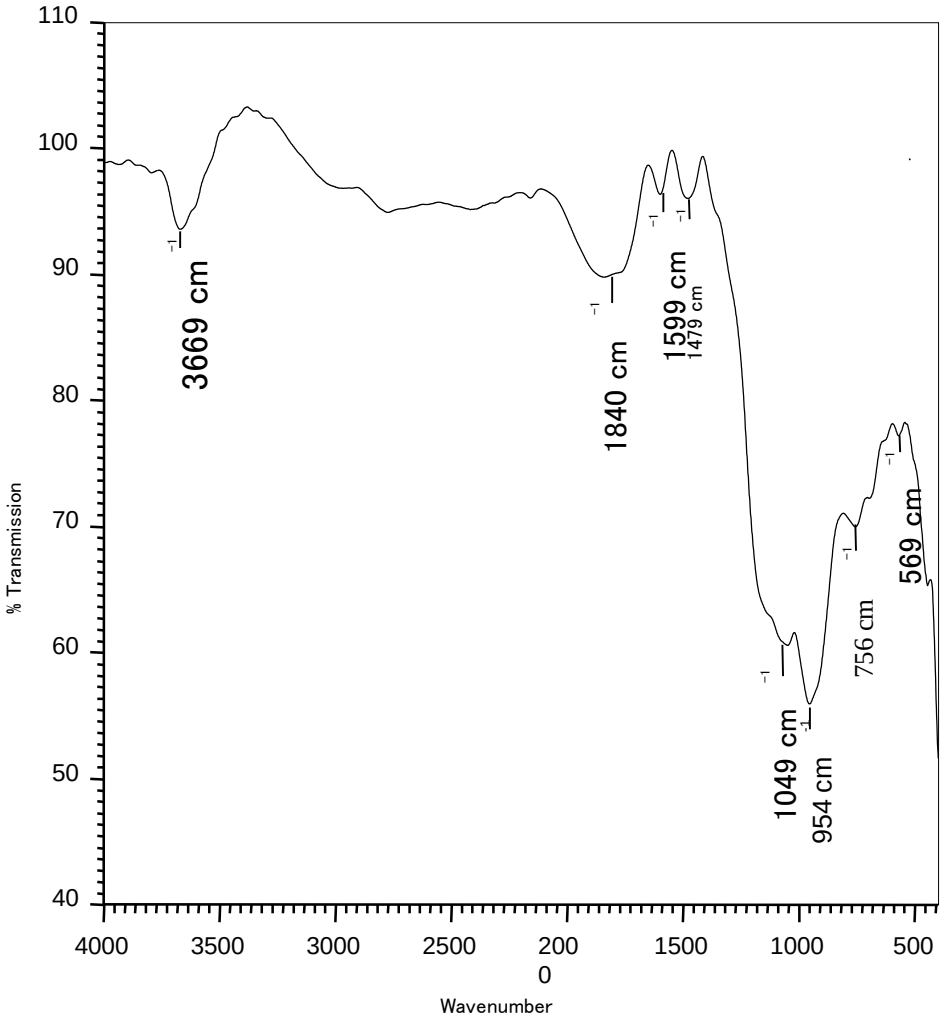
Si/Al ratio = 1.59

IR spectrum of natural scolecite zeolite



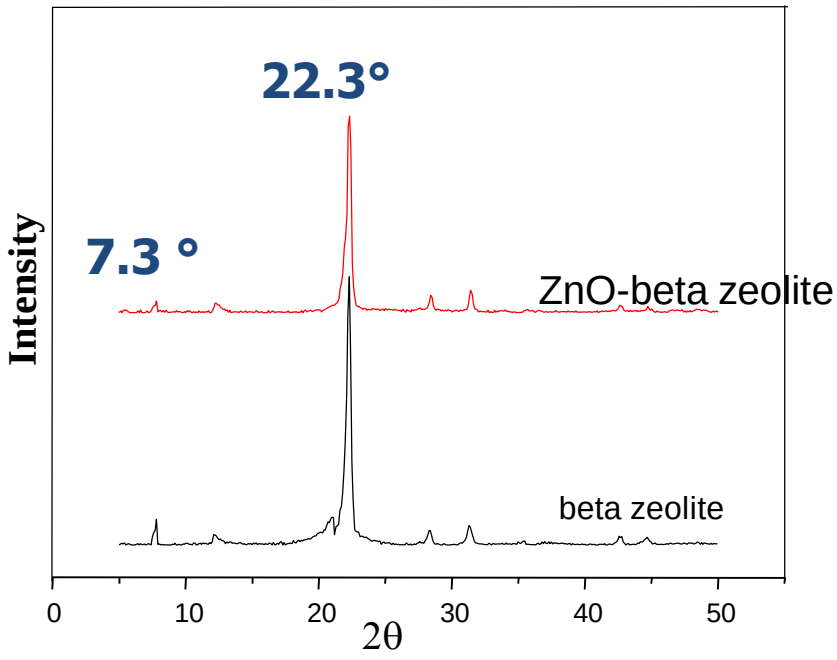
3585 – 3229 cm^{-1}	due to presence H_2O
1658, 1583 cm^{-1}	H-O-H def. band
1002 cm^{-1}	Si---O---Si or Si---O---Al str.
632 cm^{-1}	D6R vibration
496 cm^{-1}	Si---O---Si or Si---O---Al bending

IR spectrum of thermally modified scolecite zeolite



3669 cm^{-1}	Si---OH- --Al group
1840 - 1479 cm^{-1}	H-O-H deformation
1049 -- 954 cm^{-1}	Si---O---Si or Si---O---Al asy. &Sym str.
756 cm^{-1}	S4R and 4-1 ring vibration
569 cm^{-1}	D6R vibration

2. XRD pattern beta zeolite and ZnO-beta zeolite

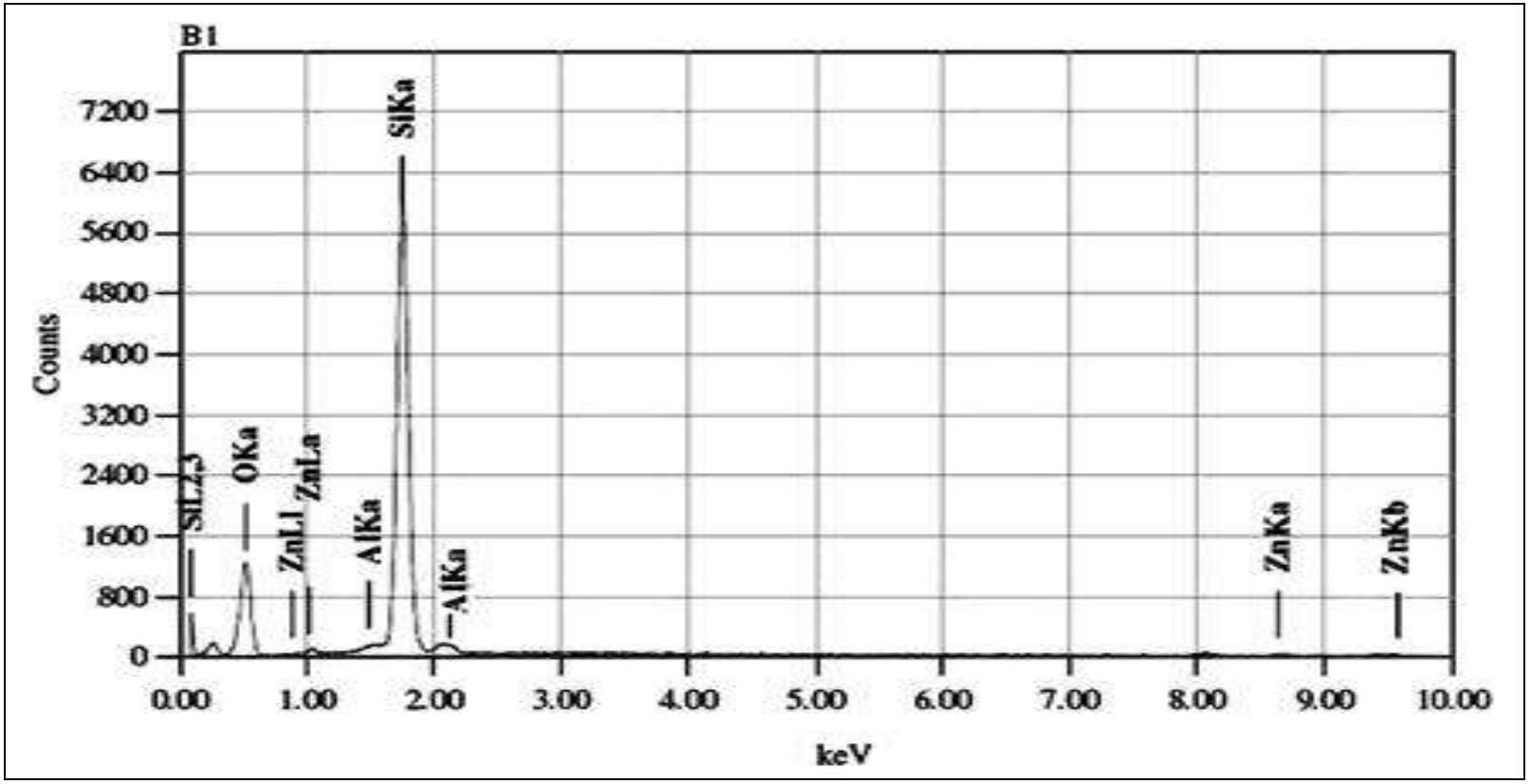


Characteristic features of beta zeolite

1. Intense XRD peaks observed at 2θ=7.3 ° and 22.3 ° which correspond to crystalline beta zeolite.

2. Calculated particle size of beta zeolite is about 10μm. It depends on the area under the peaks , larger the area under the peak smaller is the particle size.

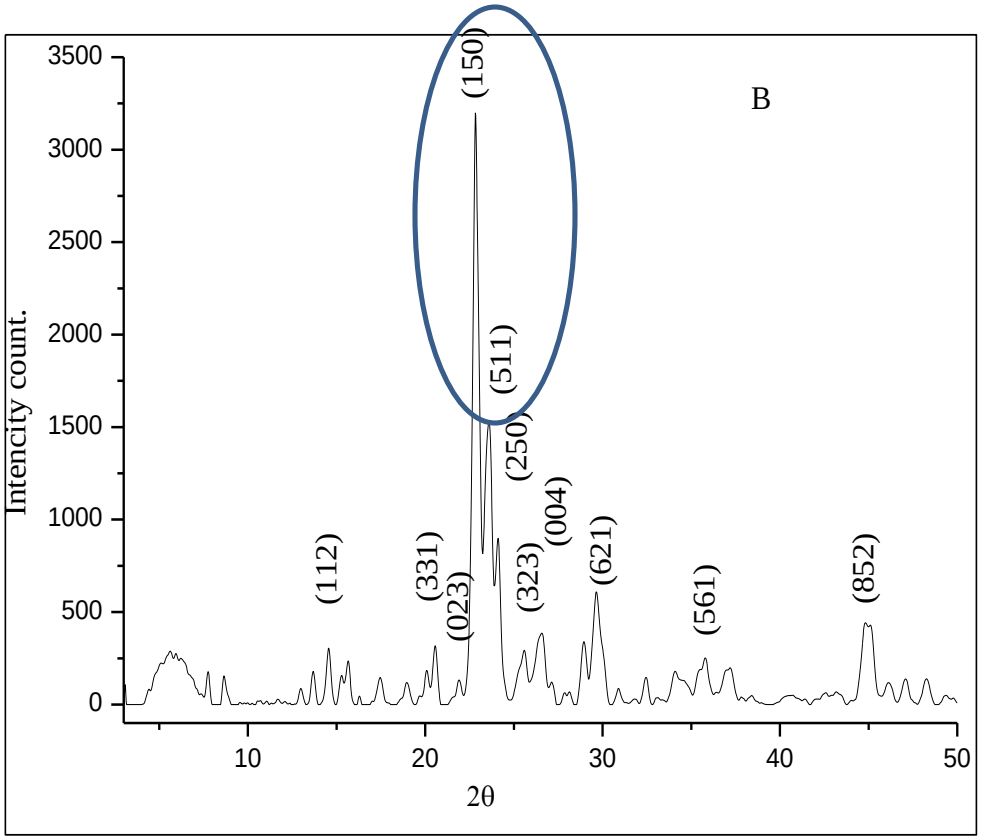
EDS analysis of ZnO-beta zeolite



1. From EDS analysis we can determine the amount of metal ions
2. 2.75 mass %. Zn is found in ZnO beta zeolite, which confirm the presence of Zn

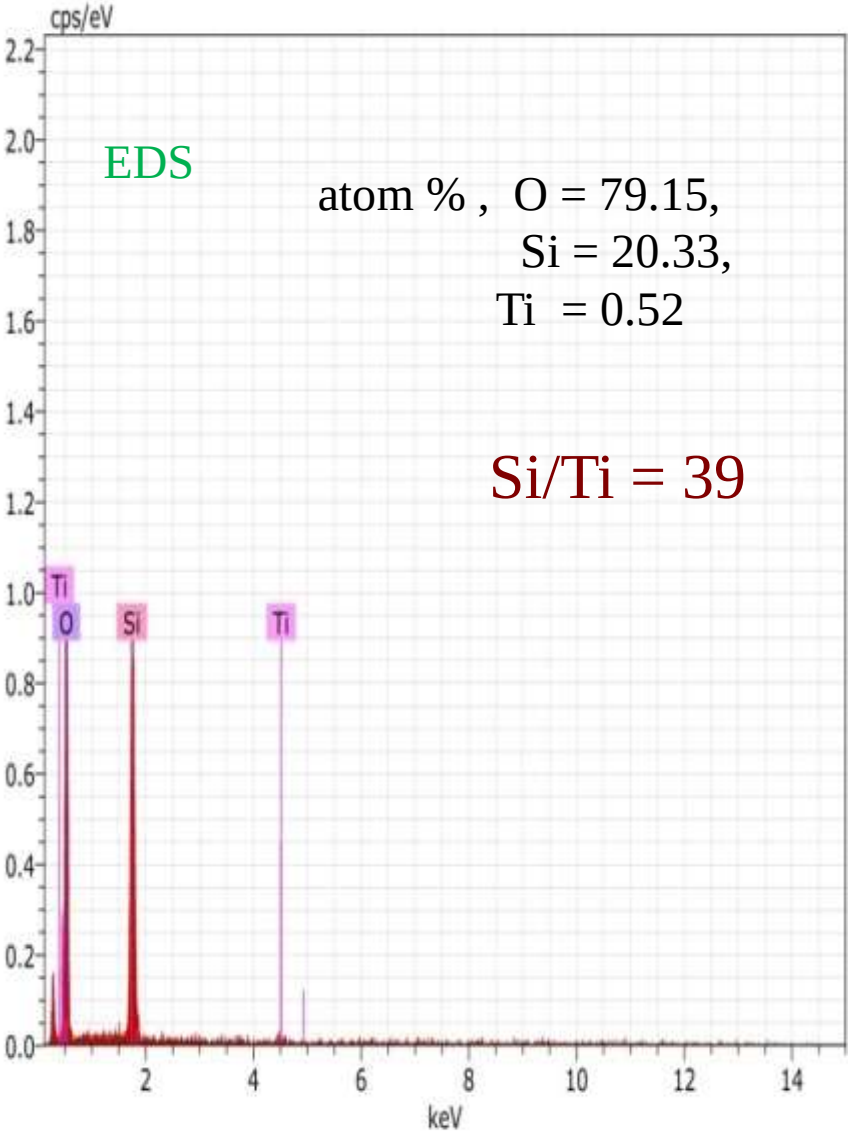
XRD analysis of TS- zeolite

XRD



1. Intense peaks at 2θ° = 14.63, 21.81, 22.76, 22.59, **24.04, 26.62** with corresponding planes (112), (023), (150), (511), (250), (004) respectively, the plane (150) and (511) indicate the presence of ordered orthorhombic TS-1 framework

EDS & SEM analysis of TS-1 zeolite

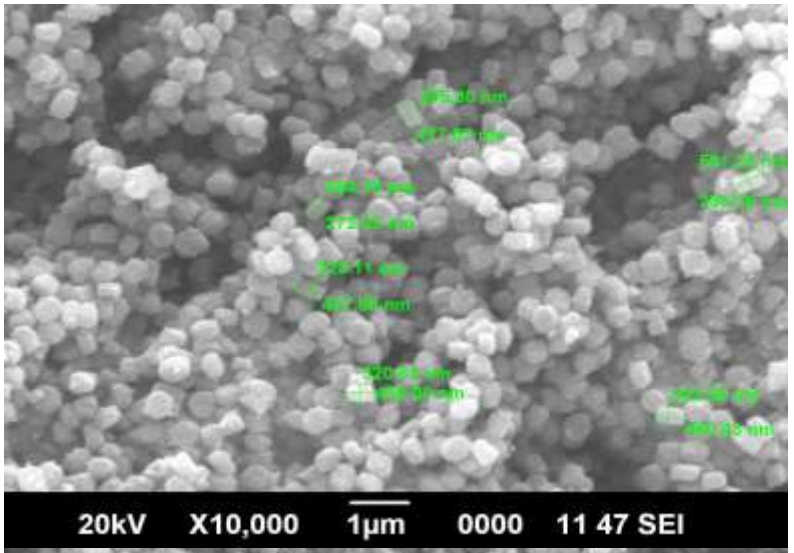


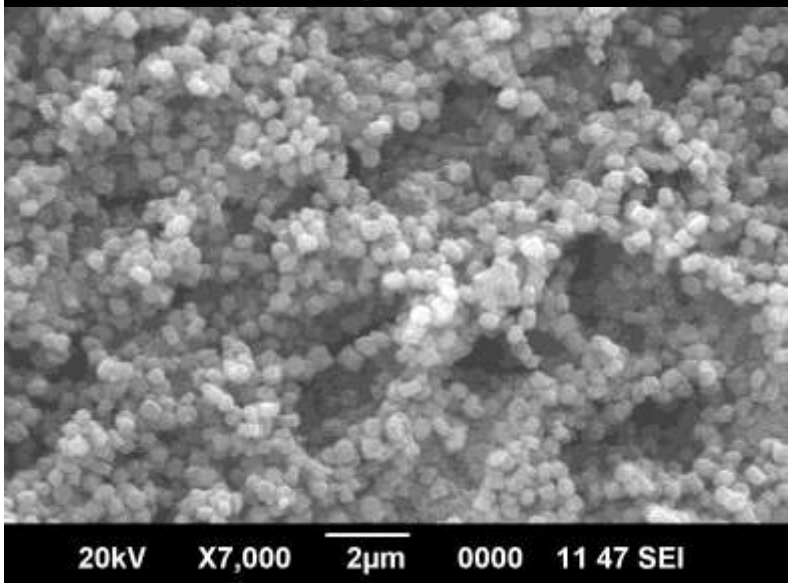
EDS

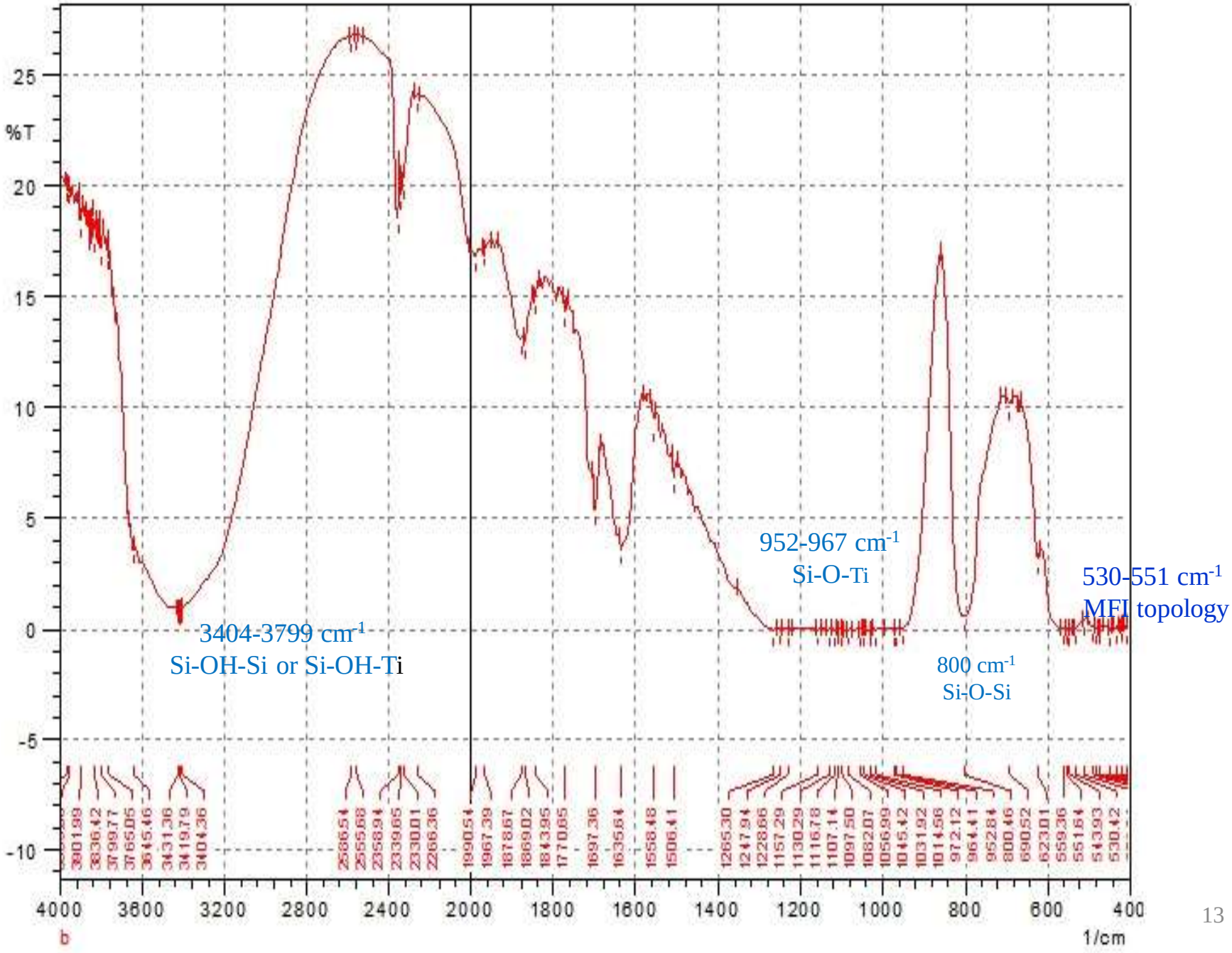
atom % , O = 79.15,
Si = 20.33,
Ti = 0.52

Si/Ti = 39

SEM






%T
25
20
15
10
5
0
-5
-10
4000
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400
1/cm
b
3404-3799 cm-1
Si-OH-Si or Si-OH-Ti
952-967 cm-1
Si-O-Ti
800 cm-1
Si-O-Si
530-551 cm-1
MFI topology

BET surface area of TS-1

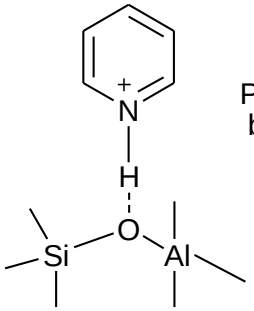
Nitrogen adsorption technique s used to determine to

BET surface Area	408.3 m^2/g
Total pore volume	0.2130 cc/ g
Average pore diameter	20.87 A°
Micro-pore volume	0.2014 cc/g
Micro-pore area	397.4 m^2/g
External surface area	10.090 m^2/g
Pore volume	0.1935 cc/ g
Pore width	14.748 A°

Qualitative analysis of Bronsted & Lewis acidic sites by using pyridine as a Probe molecule :

IR spectroscopic technique is generally used for qualitative analysis of Bronsted and Lewis acidic site using Pyridine as a basic probe molecule.. It react with Bronsted and Lewis acidic sites via formation of coordinate bond with bridged -OH group and Lewis sites.

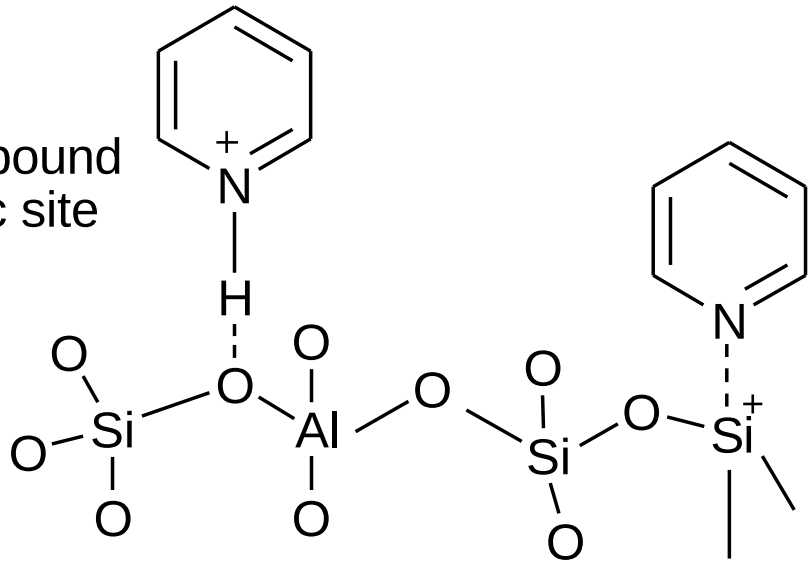
Probable interaction of pyridine with Bronsted acidic sites.



Pyridinium ion bound bronsted acidic site

Characteristic IR band : 1540 cm^{-1}

Pyridinium ion bound
bronsted acidic site

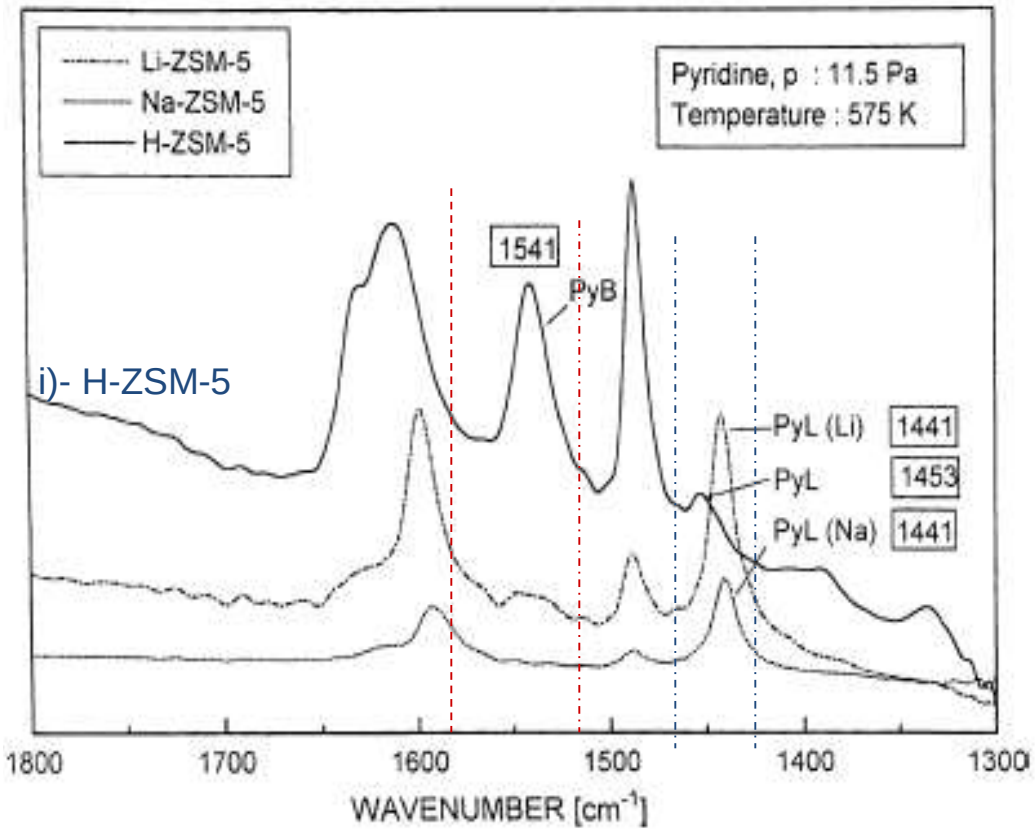


Py coodinated
with weak Lewis
site

IR band : 1450 cm^{-1}

Third IR band is called as combination band,
due both Lewis and Bronsted bound py : 1485 cm^{-1}

FTIR spectra of pyridine adsorbed into i). H-ZSM-5 ii). Li-ZSM-5, iii). Na-ZSM-5 zeolite



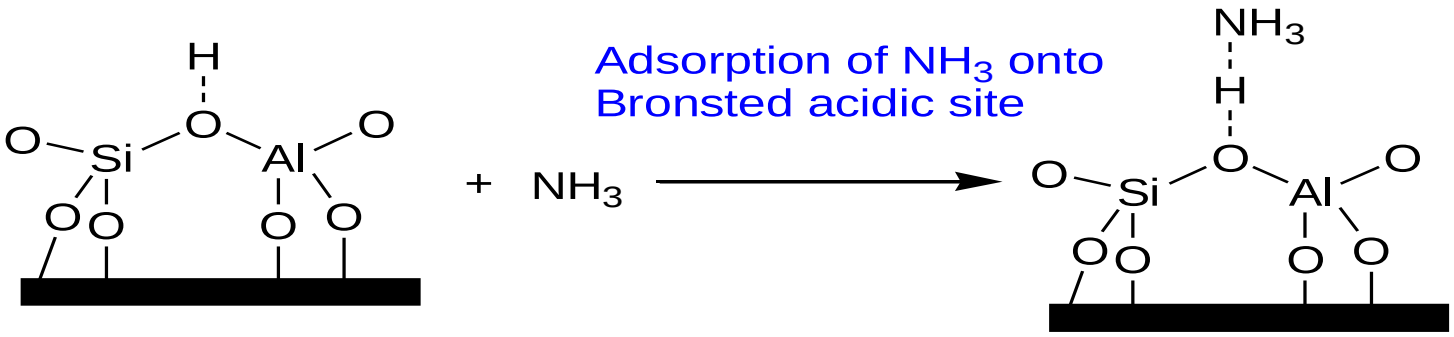
➢Pyridine adsorbed IR band near 1541 cm^{-1} confirm the presence of Bronsted acidic site in H-ZSM-5 and Bronsted acidic site does not found in Li and Na-ZSM-5

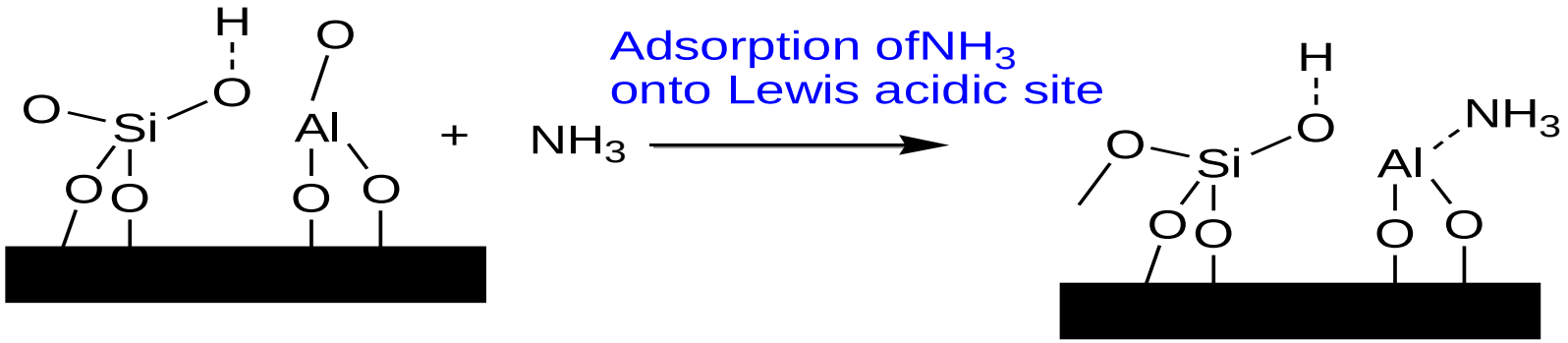
➢Py adsorbed IR band at 1441 confirm the presence of Lewis acidic site in H-ZSM, Li-ZSM, Na-ZSM

Ref:Hellmut G. Karge& Jorg Karger; Mol. Sieves 7; 235; (2008)

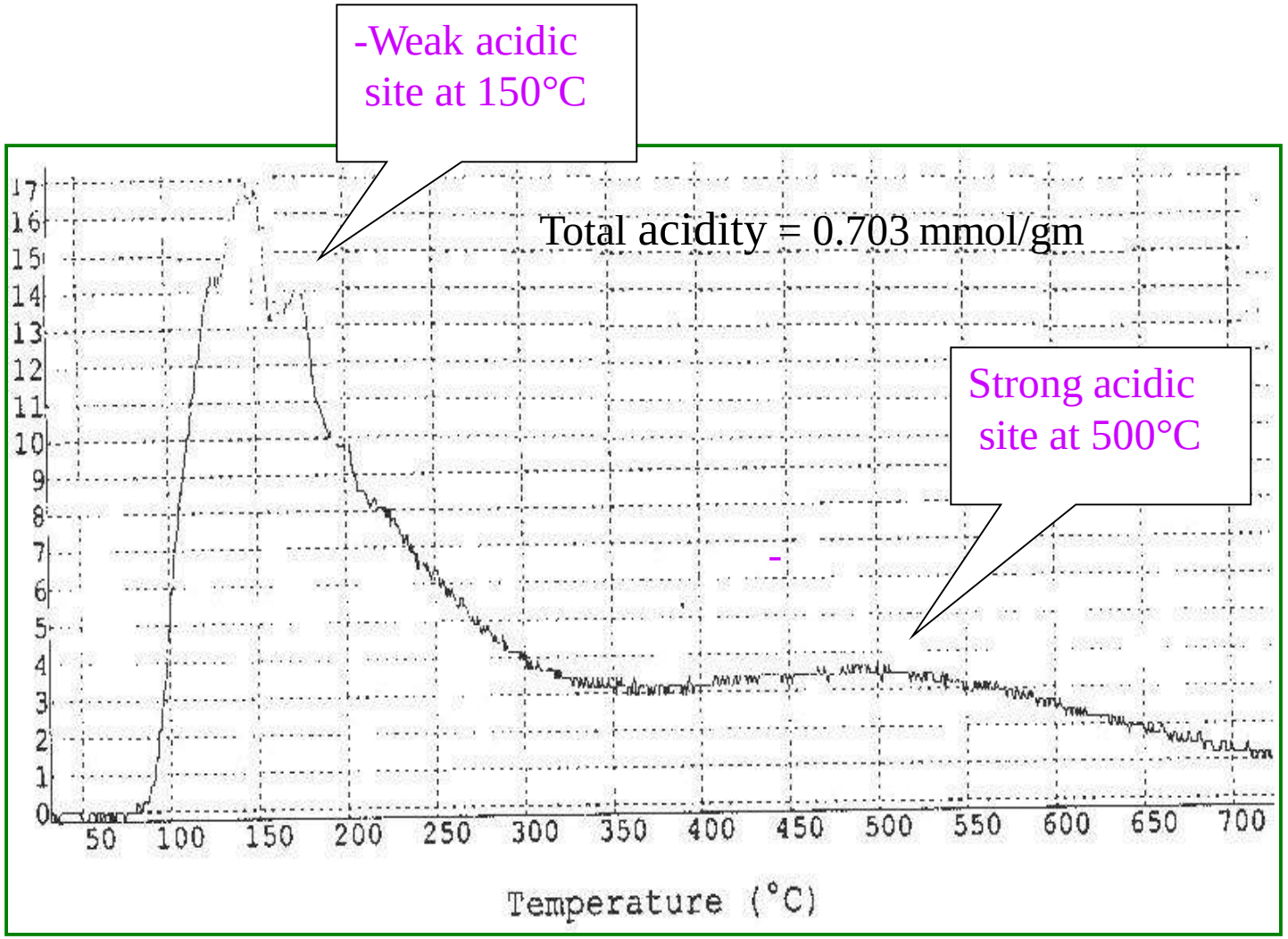
Chemioadsorption of NH_3- on a active centers of at Lewis and Bronsted acidic site

NH_3-TPD have been used to determine the nature and concentration of acidic sites of zeolites, metal oxides, mixed metal oxides. Ammonia is used as basic probe molecule. Which adsorbed onto Bronsted and Lewis sites to from coordinate bond. These are represented as :

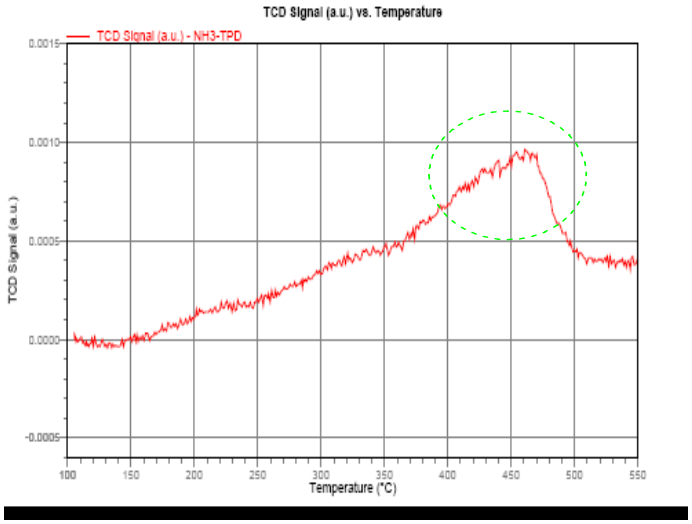




NH_3-TPD pattern for ZnO-beta zeolite.



NH_3-TPD of heat treated Natural zeolite



Natural Zeolite

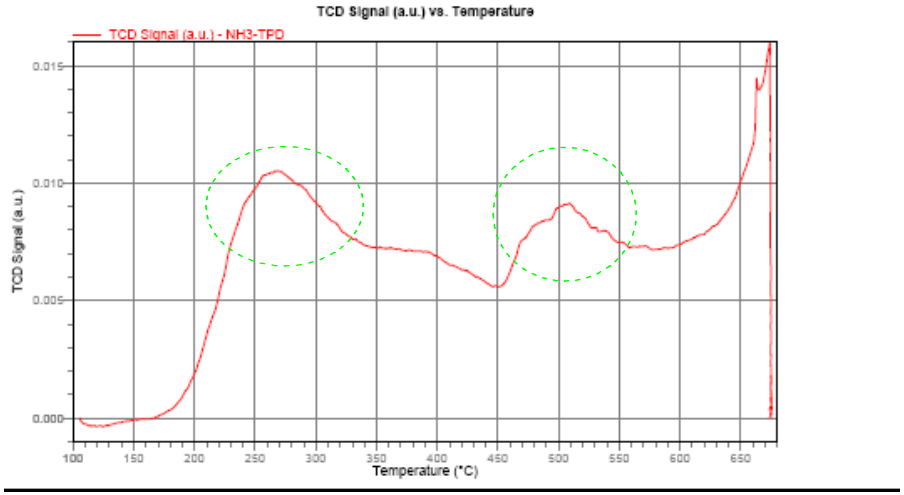
500°C

Summary Report

Experiment 1: NH3-TPD

Analysis Type: Temperature Programmed Desorption
Calibration: (CHM_0007) NH3-TPD (20cc/min Helium) TCD Calibration
Measured Flow Rate: 20.00 mL STP/min
Signal Offset: -0.13099
Signal Inverted: Yes

Peak Number	Temperature at Maximum (°C)	Volume (mL/g STP)	Peak Height
1	465.8	0.10455	0.00101



Treated Natural zeolite

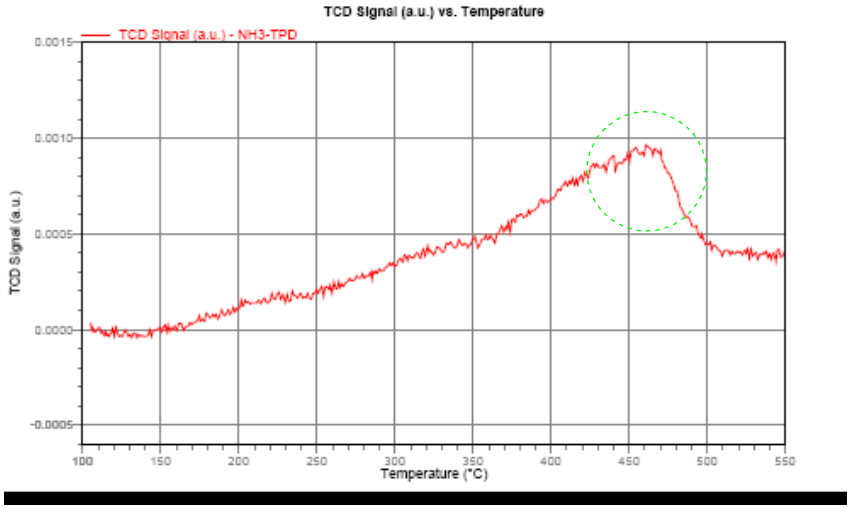
Summary Report

Experiment 1: NH3-TPD

Analysis Type: Temperature Programmed Desorption
Calibration: (CHM_0007) NH3-TPD (20cc/min Helium) TCD Calibration
Measured Flow Rate: 20.00 mL STP/min
Signal Offset: -0.13840
Signal Inverted: Yes

Peak Number	Temperature at Maximum (°C)	Volume (mL/g STP)	Peak Height
1	269.0	1.09819	0.01090
2	508.8	0.49647	0.00952

NH_3-TPD of acid treated and untreated Natural zeolite



Summary Report

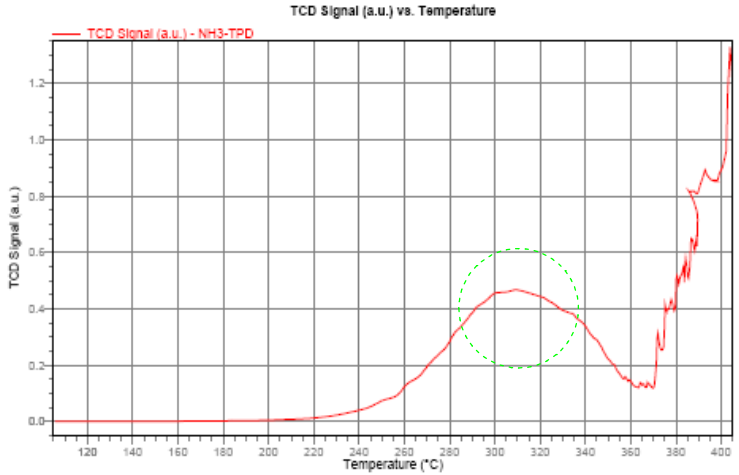
Experiment 1: NH3-TPD

Analysis Type: Temperature Programmed Desorption
Calibration: (CHM_0007) NH3-TPD (20cc/min Helium) TCD Calibration
Measured Flow Rate: 20.00 mL STP/min
Signal Offset: -0.13099
Signal Inverted: Yes

Peak Number	Temperature at Maximum (°C)	Volume (mL/g STP)	Peak Height
1	465.8	0.10455	0.00101

Natural Zeolite

H_2SO_4



Acid treated Natural zeolite

Summary Report

Experiment 1: NH3-TPD

Analysis Type: Temperature Programmed Desorption
Calibration: (CHM_0007) NH3-TPD (20cc/min Helium) TCD Calibration
Measured Flow Rate: 20.00 mL STP/min
Signal Offset: -0.14270
Signal Inverted: Yes

Peak Number	Temperature at Maximum (°C)	Volume (mL/g STP)	Peak Height
1	308.9	14.00840	0.37778

Thank You All