Materials Science Research India Volume **3(2),** 111-118 (2005)

SYNTHESIS AND CHARACTERIZATION OF 4A MOLECULAR SIEVE FROM CLAY

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(Received, 29 October, 2005)

ABSTRACT

Attempts were made to investigate compositional constraints in the synthesis of 4A molecular sieves using metakaolin from the gel composition Al_2O_3: 7.1SiO_2: 5.8 Na_2O: 150 H_2O in the temperature 100°C for 6-8h. Use of other clay materials in 4A synthesis is nullified. XRD and FT-IR spectra in framework region of 4A synthesized using metakaolin in autogeneous pressure are having similar pattern to the reported one. Scanning electron microscopic picture of the both are varies kaolin and 4A varies. MASNMR shows the presence of tetrahedral aluminium and Si:4Al, Si:3Al:Si and Si:4Si species.

Key words: 4A, kaolin, XRD, SEM, TG/DTA, FT-IR and MASNMR.

INTRODUCTION

Union Carbide[1] corporation 1959, obtained the first patent on the synthesis of a aluminosilicate zeolite, termed 4A and described as having SiO_2/Al_2O_3 = 0.5 without using template agent. However, costly chemicals such as sodium oxide, alumina and fumed silica are used in the synthesis of 4A zeolite[1]. Clays are naturally occurring cheap aluminosilicates having sheet structure. Zeolites are molecular sieves with three dimensional structure[2]. It is benefitial if we use the clays as a source in the synthesis of aluminosilicate molecular sieves. Eventhough this experiment involves commercial value, there are less studies were conducted. Here for the first time we have carried out the experiment with different clays and succeed with metakaolin.

EXPERIMENTAL

In a typical procedure to synthesize 4A using clays, 2.411g of sodium hydroxide (99%, s.d.fine, India) was mixed with 13.69g of distilled water. The mixture was stirred until the pellets dissolved fully. Metakaolin was prepared from kaolin (Ashapura Industries, Belapur, Navimumbai, India) by calcining at 800°C for 4h. 5.004g of metakaolin was added to the above sodium hydroxide solution. The whole mixture was stirred for another half hour. The resultant mixture was charged into a sealed plastic containiner. Crystallization was carried out for 6h at 100°C hydrothermally. The products were removed and washed with deionised water and the sample was dried at 110°C for 24h. The zeolite so prepared was subjected to various physicochemical characterizations. Simillar experiments were carried out with different clays, conditions are given in Table -1.

X-ray diffraction patterns were recorded on a Rigaku (D/MAX III VC) instrument in the 2θ region of 5-50°. Scanning electron microscope pictures were taken using a JEOL JSM 5200 microscope. Chemical analysis was carried out by XRF using a Rigaku 3070 X-ray Spectrometer. TG/DTA analysis was carried out using TG/DTA32 SII Seiko instruments in nitrogen atmosphere from room temperature to 1000°C. The framework IR spectra were recorded in the diffuse reflectance mode using 300 : 1 ratio sample in KBr (Nicolet 60SXB). MASNMR spectra were recorded in the solid state with a Bruker DRX 500 spectrometer operating at a field of 11.7 Tesla. ^{27}Al spectra were recorded at a frequency of 130.3 MHz, with a pulse length of 2ms and a spinning speed of 3-5 KHz. ^{29}Si NMR spectra were recorded at 99.3 MHz, 2μs (45°) pulse width

Table - 1: Synthesis of 4A from clay gels

S. No.	Gel composition	Pressure	Si - source	Product
1.	Al_2O_3: 7.097SiO_2: 5.761 Na_2O: 150 H_2O	autogeneous	Metakaolin	4A
2.	Al_2O_3: 7.097SiO_2: 5.761 Na_2O: 150 H_2O	atmospheric	Metakaolin	4A + kaolin
3.	Al_2O_3: 7.097SiO_2: 5.761 Na_2O: 150 H_2O	atmospheric	Kaolin (China clay)	Kaolin
4.	Al_2O_3: 7.097SiO_2: 5.761 Na_2O: 150 H_2O	atmospheric	Autopulgite	Autopulgite
5.	Al_2O_3: 7.097SiO_2: 5.761 Na_2O: 150 H_2O	atmospheric	Ballclay	Ballclay

Temperature = 80 - 100°C and time = 3-6h
NaOH = 2.411 (H_2O/Na_2O = 30), H_2O = 13.69 ml and metakaolin (5.004g, SiO_2/H_2O = 100)

and repetition time of 2s. Tetramethylsilane (for silicon) and 1M $Al(NO_3)_3$ solutions (for aluminium) were used as standards.

RESULTS AND DISCUSSION

To determine the compositional range of the hydrogel that would yield a 4A molecular sieve, synthesis runs were carried out from the hydrogel system whose oxide mole composition was Al_2O_3: 7.097SiO_2: 5.761 Na_2O: 150 H_2O at 100°C for 6h. Crystallization at autogeneous pressure using metakaolin gives pure 4A. Same with atmospheric pressure gives 4A along with kaolin mixture. Kaolin, Autopulgite and ball clay gives their respective compounds with less intensity and 4A is not formed (Table - 1).

The different phases (tabulated in Table -1) obtained during the present synthetic studies are identified on the basis of their X-ray diffraction pattern. Fig. - 1 shows a typical XRD pattern take at 8°/min scan for the product obtained gel composition Al_2O_3: 7.1SiO_2: 5.8 Na_2O: 150 H_2O crystallized at 100°C for 6h under autogeneous pressure. This X-ray pattern characterizes the product to be almost pure 4A. The sample prepared was step scanned with an internal standard. It is seen that the agreement is excellent with standard one indicating the complete crystallization had occurred.

Scanning electron micrographs of kaolin and 4A were given in Fig. - 2 and correlate with the XRD patterns of Fig. - 1. The crystal habit of the 4A crystals synthesized using no template seems to be rather different to that observed with the crystal of kaolin. However Fig. - 2b showing intergrown spheroids (4A, 1µm) crystals and small spheroid sieves (0.5µm) with the uniform size, indicates that the product is of high purity and it is not contaminated with impurity phases.

Fig. - 3 shows the thermogravimetric and differential thermometric curves for both the kaolin and 4A samples. Curve a represents the kaolin sample showing a two step weight loss from room temperature to 600°C, which is due to loss of the physisorbed and chemisorbed water. The total % loss in weight for this sample is 17.018. Curve c, for 4A sample prepared under autogeneous pressure, shows a single stage loss in weight up to 400°C amounting to 29.103%. The entire loss in weight is due to removal of water from the zeolite cavity. Both sample when calcined up to 823K and allowed to cool to room temperature were found to absorb ~12.5% water on equilibrating at room temperature. This indicates that sample kaolin is less stable in structure compared to 4A.

The infrared spectrum in the framework region (400-4000 cm^{-1}) for kaolin and 4a are shown in Figure 4. Kaolin shows complicate vibrations at 430(m), 470(m), 540(m), 696(w), 754(vw), 795(vw), 912(m), 1008(vsh), 1032(s), 1115(w) and 3620(m) cm^{-1} bands. 4A contains 430(vsh), 457(m), 534(w), 658(w), 691(vw), 851(wsh), and 989(s) cm^{-1} vibrations. They are assigned[3] to poreopening, double ring, T-O-T (T = Al or Si) bending, symmetric and asymmetric vibrations. Silanol groups are appeared in kaolin and not in 4A.

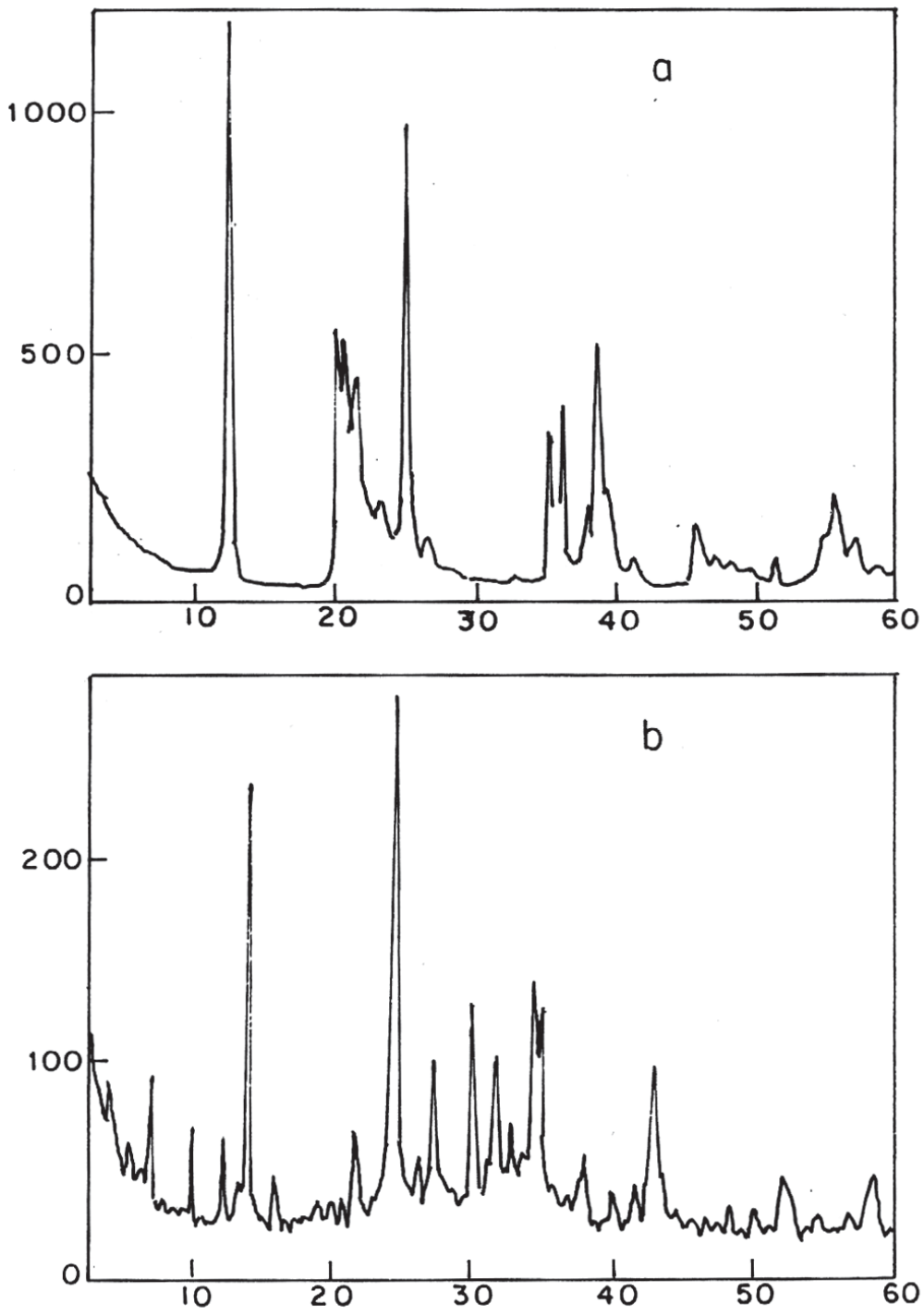

Fig. - 1 : X-ray diffraction pattern of a) kaolin and b) 4A

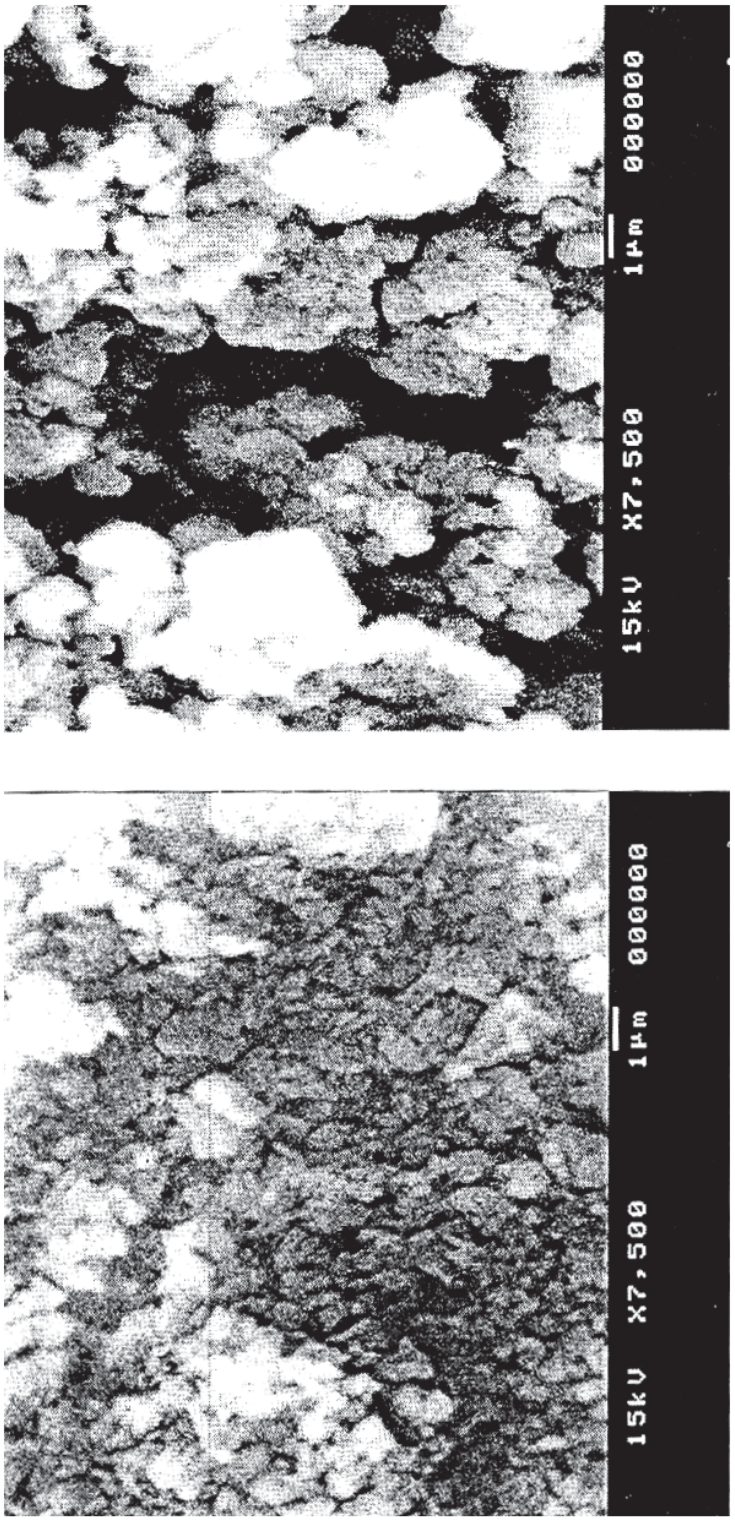

Fig. - 2 : Scanning electron microscopic picture of a) kaolin and b) 4A

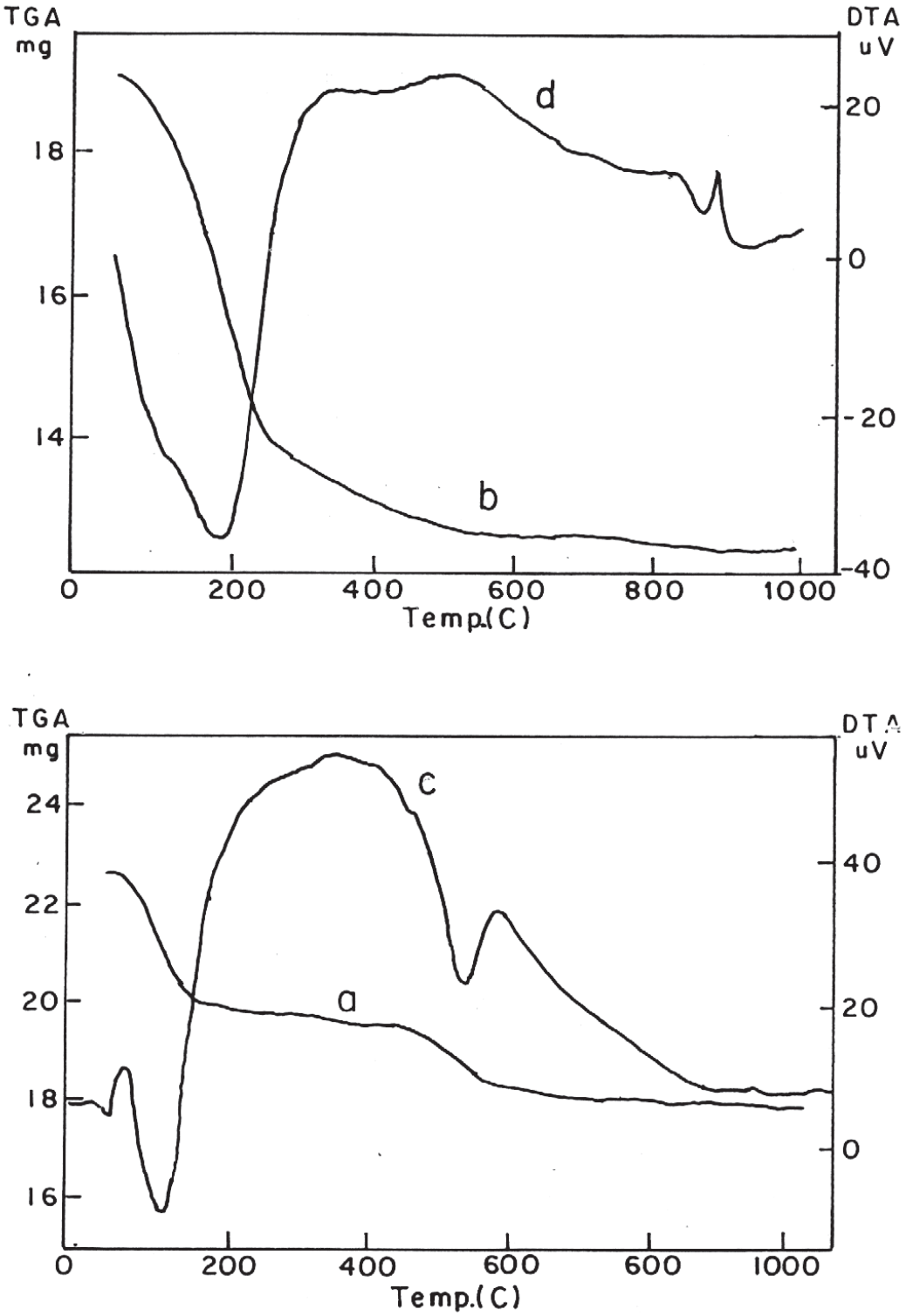

Fig. - 3 : TG (b,d)/DTA(a,c) analysis of a,b) kaolin and c,d) 4A

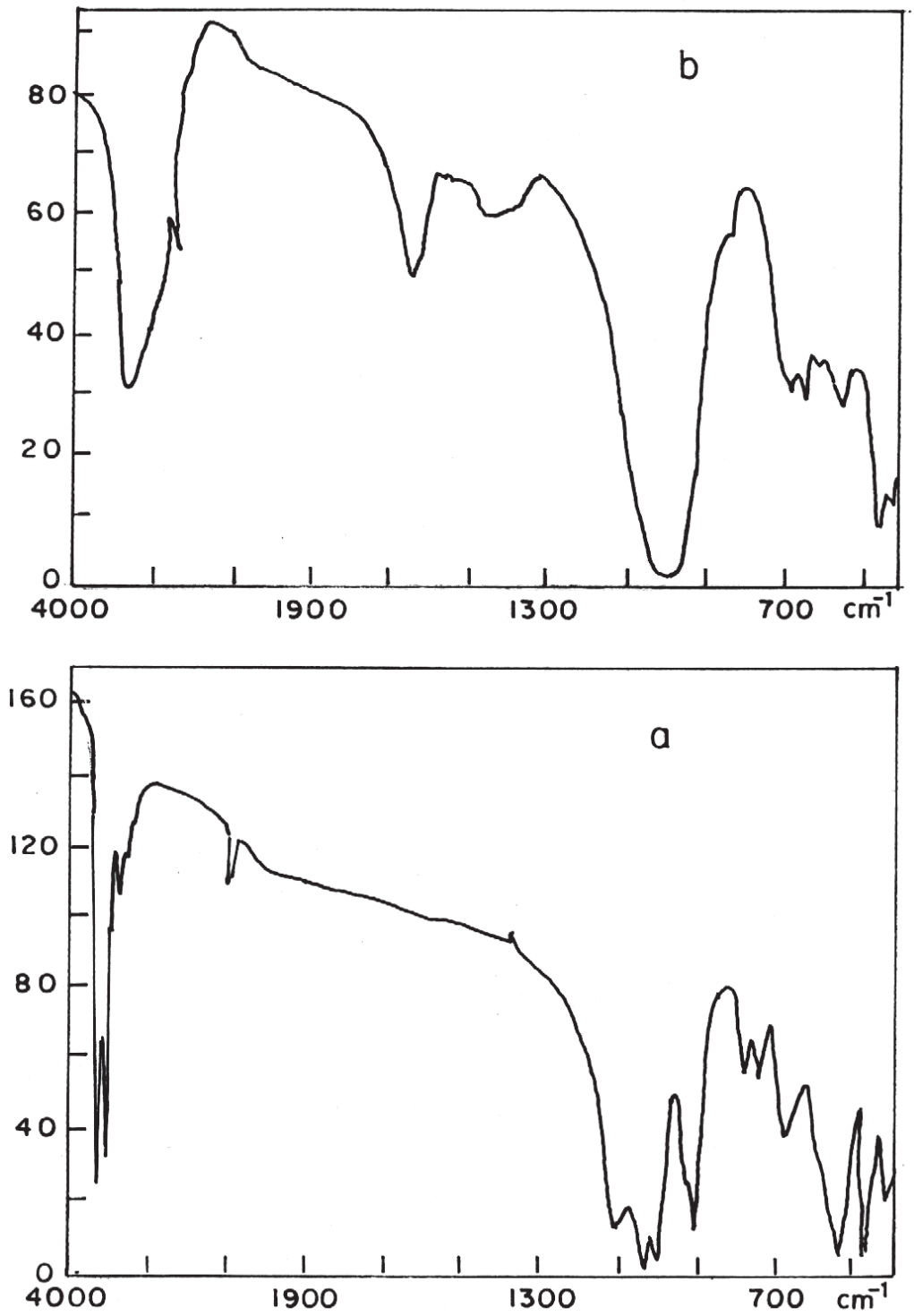

Fig. - 4 : FT-IR spectra of a) kaolin and b) 4A

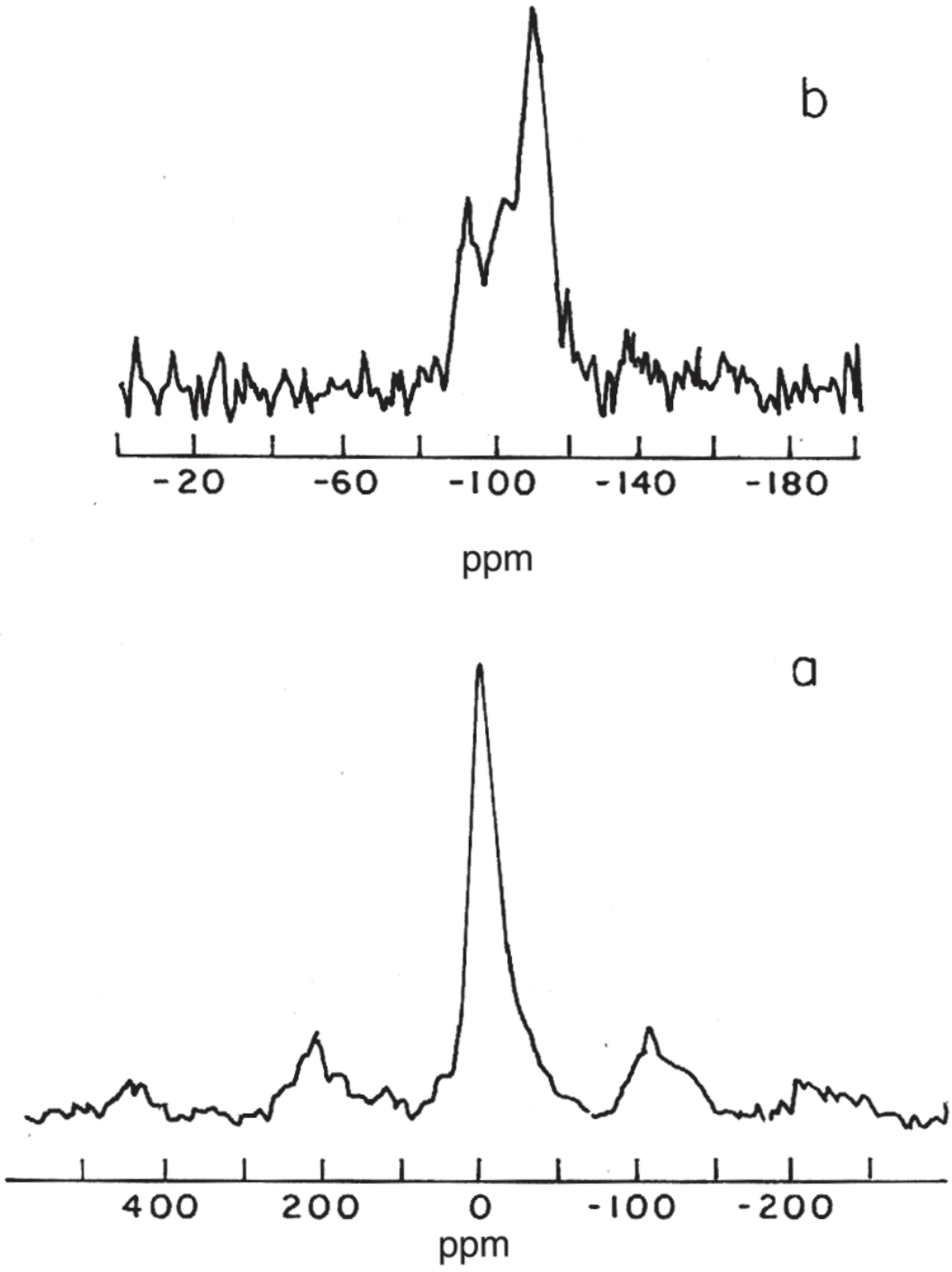

Fig. - 5 : ^{27}Al (a) and ^{28}Si (b) MASNMR spectra of 4A

^{27}Al and ^{28}Si MAS NMR spectra of the 4A sample are shown in Fig. 5. The ^{27}Al NMR spectrum of the sample shows two signals. The dominant line at –1.081 ppm has to be ascribed to octahedrally coordinated aluminium atoms bonded via oxygen to four phosphorous atoms[4]. The value of the chemical shift fits well in the range observed for other aluminosilicates[5-8].

An ^{29}Si MAS NMR spectrum of the 4A sample is shown in Fig. 5. In accordance with other authors[9,10], we assign the four lines –93, -97 and -111 ppm to silicon surrounded by four AlO_4 tetrahedra and to silicon surrounded by $3AlO_4$ and $3AlO_4$ respectively. From the spectral intensities is follows that only ca. 25wt% of the aluminium was found by chemical analysis of the samples are incorporated as monomeric aluminium into the 4A framework. Only the isolated aluminium atoms in the framework can produce Bronsted acidity.

Conclusion

Attempts were made to investigate compositional constraints in the synthesis of 4A molecular sieves using metakaolin from the gel composition Al_2O_3: 7.1SiO_2: 5.8 Na_2O: 150 H_2O in the temperature 80-100°C for 3-6h. Use of other clay materials in 4A synthesis is nullified. XRD and FT-IR spectra in framework region of 4A synthesized using metakaolin in autogeneous pressure are having similar pattern to the reported one. Scanning electron microscopic picture of the both are varies kaolin and 4A varies. MASNMR shows the presence of tetrahedral aluminium and Si:4Al, Si:3Al:Si and Si:4Si species

ACKNOWLEDGEMENT

The author is thanking the CSIR, New Delhi for Research Associateship.

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